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Papers from the Torquay Conference

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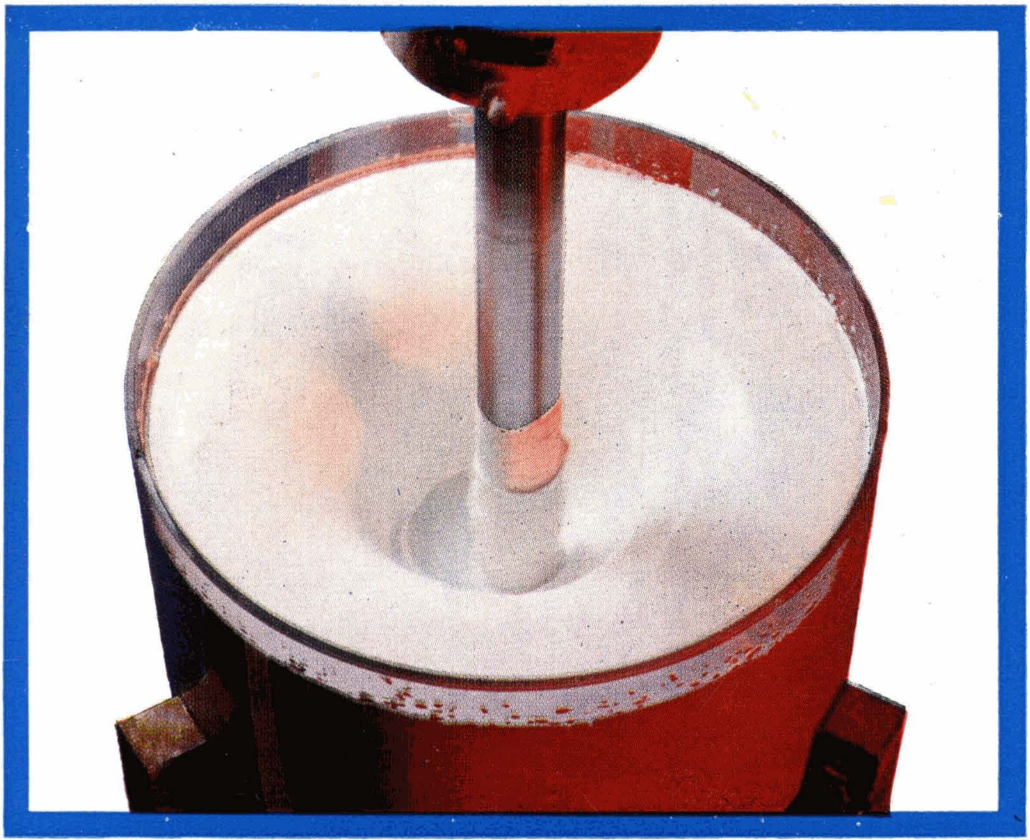

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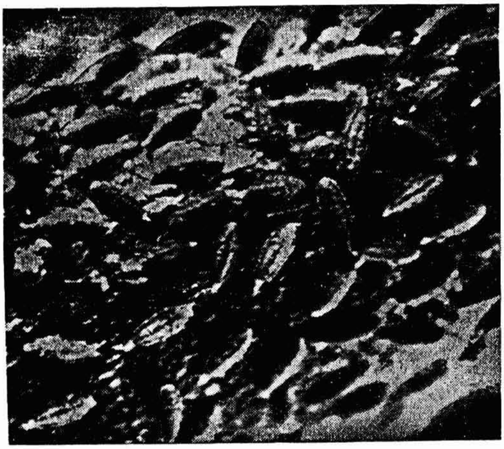

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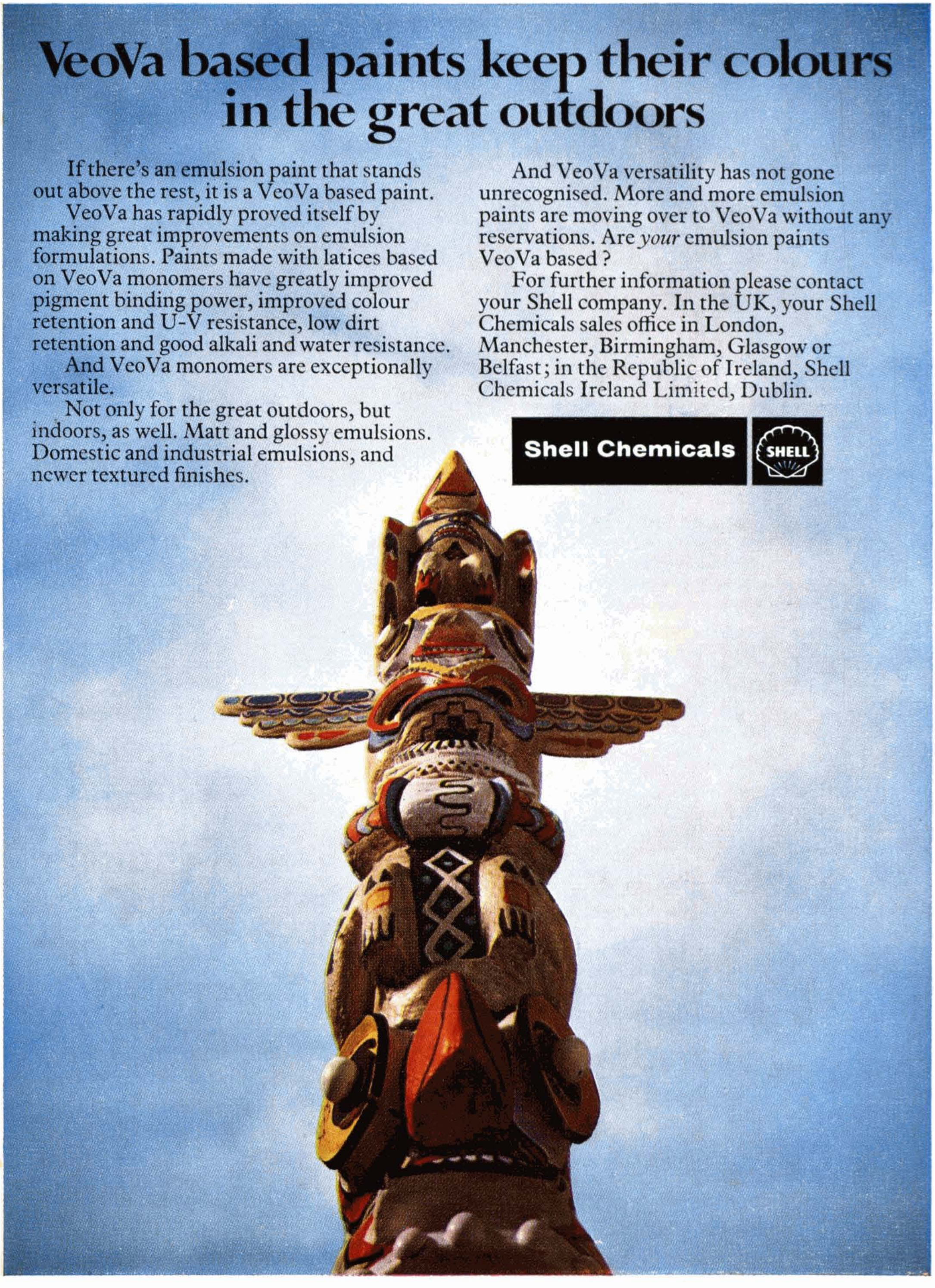

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Editorial correspondence should be addressed to the Hon. Editor, *JOCCA*, 49 Elms Drive, Kirk Ella, Hull HU10 7QH.

General correspondence should be addressed to:

R. H. Hamblin, M.A., F.C.I.S.,
Director & Secretary,

Oil & Colour Chemists' Association,
Wax Chandlers' Hall, Gresham Street,
London EC2V 7AB. (Tel.: 01-606 1439)
Telex: 883711 Grams: Oil Colour London

Assistant Secretary: N. S. Pearce, A.C.I.S.
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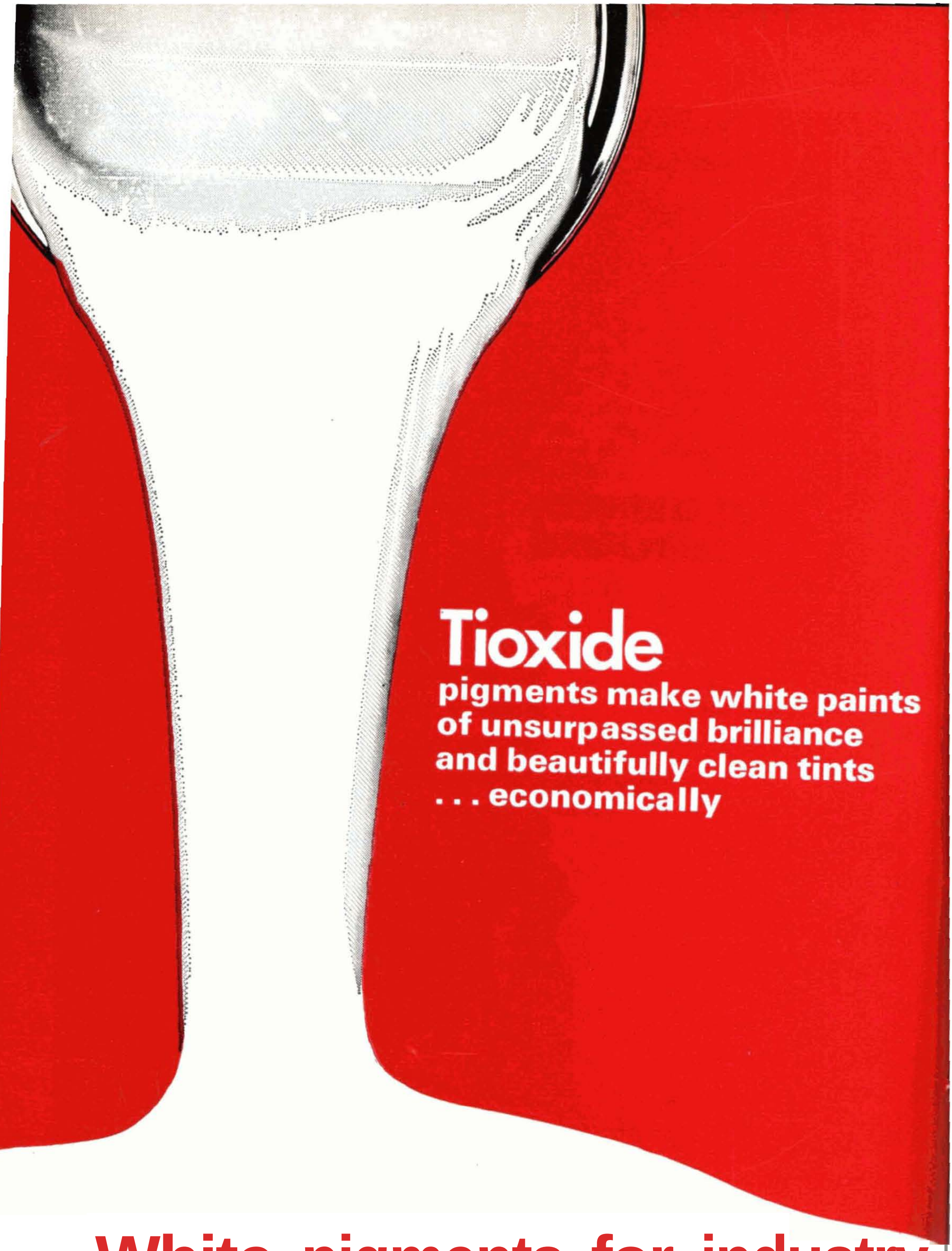
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Transactions and Communications

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Wax Chandlers' Hall, Gresham Street, London, EC2V 7AB

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Transactions and Communications

Opacity of roller coatings: Part II. Theoretical analysis*

By D. F. Tunstall and D. G. Dowling

Tioxide International Limited, Central Laboratories, Stockton-on-Tees,
Teesside TS18 2NQ

Summary

A fundamental study of the influence of internal and external surface reflections on the opacity of thin paint films has been made, and an equation relating opacity to the reflectance characteristics of the film surfaces (the upper surface and the substrate) has been derived. It is shown how the true Kubelka-Munk back-scattering coefficient is obtained from the experimental data and the effect of sizing a metal surface is examined on a quantitative basis.

Keywords

Types and classes of coating	*Properties, characteristics and conditions primarily associated with dried or cured films*
roller coating finish	opacity reflectance

L'Opacité d'émaux couchés. Deuxième partie: Analyse théorique

Résumé

On a effectué une étude fondamentale sur l'influence qu'exercent les réflexions aux surfaces interne et externe sur l'opacité de feuils minces. On a dérivé une équation entre l'opacité et les caractéristiques reflecteurs des surfaces du feuil (c'est-à-dire, la surface d'en haut et celle-la à l'interface feuil/subjectile). On démontre comment obtenir le vrai coéfficient Kubelka-Munk de "back-scattering" à partir des données expérimentales. On examine, au point de vue quantitatif, l'effet d'une couche primaire de vernis appliquée à la surface métallique.

Opazität von durch Bandlackierung Aufgetragenen Beschichtungen Teil II. Theoretische Analyse

Zusammenfassung

Eine fundamentale Untersuchung des Einflusses von inneren und äusseren Oberflächenrückstrahlungen auf die Opazität dünner Lackfilme wurde vorgenommen, und dabei eine Gleichung abgeleitet, in welcher die Opazität mit den Reflexionscharakteristika der Filmoberflächen (der oberen Fläche und dem Substrat) in Beziehung steht. Es wird gezeigt, wie man den echten Kubelka-Munk Rückstreukoeffizient von den experimentell gefundenen Werten erhält. Die Auswirkung der Absiegelung einer Metalloberfläche wird quantitative geprüft.

Непрозрачность валиковых покрытий Часть II. Теоретический анализ

Резюме

Дается фундаментальный анализ влияния внутренних и внешних поверхностных отражений на непрозрачность тонких красочных пленок и выводится уравнение связывающее непрозрачность с характеристикой отражаемости поверхностей пленок (верхней поверхности и субстрата).

Показано каким образом можно получить истинный коэффициент обратного рассеяния Кубельки-Мунка из экспериментальных данных и анализируется влияние проклейки металлической поверхности на основе количественной оценки.

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*Presented at the Torquay Conference on 6 May 1971.

Introduction

The measured reflectances of a selection of roller coatings on a variety of substrates have been discussed in part I of this paper. The relative importances of pigment dispersion, pigment concentration, film thickness and substrate reflectance have been found by statistical analysis. To appreciate fully the effects of these variables, a theory is required by which their relative roles can be expressed in a quantitative manner.

The approach to the problem is, of course, essentially different from that used in part I. The statistical analysis brings to light interactions that would not normally be noticed. The theoretical approach, however, must be restricted to analysis of the major variables. Provided these are not too numerous, a basic theory can be established and then perhaps refinements can be made. It may then be possible to obtain explanations for some of the more unexpected interactions found from the statistical analysis.

In this part of the paper, a simple but soundly based practical equation will be derived that fully describes the optical properties of white roller coatings in terms of the statistically determined major variables. The theory is based on the sometimes maligned but much used two constant theory of Kubelka and Munk (K-M)[1]. Modifications to the basic theory are necessary to obtain the desired equation. The final expression, though relatively simple in form, can be applied to a wide range of white pigmented systems.

The equation will be used to analyse the reflectance data and it will be shown how it allows adequately for the major variables of film thickness and substrate reflectance. This will be followed by a quantitative analysis of the substrate reflectances to assess the effect of sizing on reflectance. Finally, a summary of the practical expressions necessary to determine the reflectance of a paint film on an optically flat metal surface, sized or unsized, will be given.

Theoretical derivation of the reflectance equation

Most of the practical problems associated with the use of K-M theory are due to neglect of the original postulates laid down for its application. The original K-M[1] equations for reflectance, R, and transmittance, T, apply only to a planar scattering system of infinite extent, having no specularly reflecting boundaries and illuminated with diffuse light. They are as follows:

$$R = \frac{\sinh bSX}{a \sinh bSX + b \cosh bSX} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$T = \frac{b}{a \sinh bSX + b \cosh bSX} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where S = back-scattering coefficient for diffuse light

X = film thickness

and a and b are defined by

$$a = 1 + K/S, \quad b = (a^2 - 1)^{\frac{1}{2}}$$

where K = absorption coefficient for diffuse light.

Three additional constants must be introduced before these equations can be applied to practical paint systems. These will be considered individually.

Substrate reflectance

This modification has already been introduced by Kubelka and Munk. However, the complexity of the substrate reflectance is generally not appreciated. It should be remembered that two types of reflectance can occur from the substrate of a film. The diffuse light transmitted through the paint first encounters a boundary between the paint and the bulk substrate. This boundary introduces a specular reflectance for the diffuse light, its magnitude depending on the relative refractive indices of the paint and the bulk substrate. Light that is transmitted across this boundary can then be reflected by scattering processes within the substrate.

Generally, therefore, the reflectance of a substrate measured in air is not the value that applies when a paint film is laid on that substrate. This is due to major changes in relative refractive index at the surface of the substrate and hence changes in the specular reflectance for diffuse light at the paint/substrate boundary. An example of the magnitude of this effect has been given by Blevin[2]. The substrate reflectance of roller coatings on metal substrates depends entirely on this effect. Light that is transmitted into the metal is completely absorbed.

In this paper, the total effective reflectance at the substrate boundary of the roller-coating is denoted by r_2. Equation (1) is modified by its inclusion to give

$$R = \frac{(1 - ar_2)\sinh bSX + br_2\cosh bSX}{(a - r_2)\sinh bSX + b\cosh bSX} \quad \dots\dots\dots\dots\dots\dots(3)$$

It can be expressed in more familiar form by re-arrangement, i.e.

$$R = \frac{1 - r_2(a - b\coth bSX)}{a - r_2 + b\coth bSX} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(4)$$

The top surface reflectance

This modification is a major one that is still often ignored in practical paint film technology. The air/paint boundary is generally associated optically with gloss and many people are familiar with the correction that should be applied to reflectance values to eliminate the gloss effect i.e. reflectance of the incident light at the air/paint boundary before penetration of the light into the film. It will be shown later how the correction for this effect is automatically taken care of in the analysis of reflectance values.

However, a much more important effect occurs at this surface. Light that is scattered back towards the paint/air boundary from within the film experiences a substantial reflection at the boundary. This can be as much as 60 per cent, due mainly to total internal reflection, since the light is almost perfectly diffuse and is incident on the boundary from the high refractive index medium.

Saunderson[3] applied a correction for this effect in his work on the colour of plastics. However, the value of 0.40 that he derived by trial and error for the internal surface reflectance of the diffuse light is not, in fact, a true measure of the boundary reflectance. A similar value has been obtained by Bridgeman[4].

Both workers, in fact, used the same method for determining the constant. This involves finding a value which gives corrected reflectances that then give K/S ratios approximately proportional to colourant and pigment concentrations. Although this approach is satisfactory for improving colour matching techniques, it is no use when absolute values of the variables are desired. The K/S ratios obtained using the above method are about two to three times larger than the true values.

The errors arise from ignoring the directional nature of the incident light. This effect will be discussed in the next section, where an equation will be given that includes the internal surface reflectance (r_1) of the diffuse light.

Parallel incident light

Paint media generally have a refractive index of about 1.5. Since glossy films tend to have a clear layer of resin at the air surface, all light transmitted into the film undergoes refraction at the boundary prior to being scattered by the pigmented bulk of the film. Thus, irrespective of its angle of incidence, any light transmitted into the film is initially confined to the forward cone of semi-angle equal to the critical angle of the boundary i.e. 40-45°. In effect, the incident light penetrates further into the film than K-M theory would predict, so giving a lower reflectance than expected. For films containing rutile TiO_2 this amounts to a reflectance reduction of about 3 per cent.

A relatively simple correction, in the form of a constant, D, will be introduced into the equation for reflectance to allow for this effect. The new equation is derived by assuming that a small depth of film is required to diffuse the incident parallel light before back scattering commences. Although this assumption might appear to be rather crude, detailed theoretical considerations have shown that it is reasonable. Experimental application of the final equation in a variety of systems has proved most successful.

The derivation of the equation including the quantities D and r_1 is lengthy and is not included here. The final reflectance equation is:

$$R = \frac{(1 - r_1)\,[(1 - ar_2)\sinh b(SX - D) + b\,.\,r_2 \cosh b(SX - D)]}{[(a - r_2) - r_1\,(1 - ar_2)]\sinh bSX + (1 - r_1 r_2)\,b\cosh bSX} \quad ..(5)$$

The nature of the correction for parallel incident light restricts the use of this equation to reflectance greater than about 20 per cent.

Approximations for white films

Equation (5) is obviously not very suitable for practical use, owing to its complex form. Fortunately, however, quite drastic approximations can be made for application to white films. The ratio K/S is small, i.e. generally less than 10^{-4}, so permitting "a" to be taken as unity. Since "b" is also low in value (i.e. < 0.02), bSX is generally small enough to allow the following approximations to be made:

$$\sinh bSX \longrightarrow bSX; \; \cosh bSX \longrightarrow 1.$$

These are valid to within 1 per cent under the following conditions:

$$bSX < 0.24 \text{ for } \sinh bSX \longrightarrow bSX$$

$$bSX < 0.15 \text{ for } \cosh bSX \longrightarrow 1.$$

These approximations are particularly acceptable for application to roller coatings, since SX values are generally lower than for normal decorative paints.

Equation (5) can now be rewritten as follows:

$$R = \frac{(1 - r_1)(1 - r_2)(SX - D) + (1 - r_1)r_2}{(1 - r_1)(1 - r_1)\,SX + (1 - r_1 r_2)}$$

By further re-arrangement this equation gives

$$R = \frac{SX + M}{SX + N} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

where

$$M = \frac{r_2}{(1 - r_2)} - D.$$

$$N = \frac{(1 - r_1 r_2)}{(1 - r_1)(1 - r_2)}$$

This equation is mathematically straightforward, easy to use and, as will be shown later, is very satisfactory for accurately characterising white roller coatings. By putting $r_1 = r_2 = D = O$ in equation (6), the familiar approximate *K-M* expression

$$R = \frac{SX}{SX + 1}$$

is obtained.

Experimental factors

Absolute reflectance

Equation (6) gives the basic relationship between the absolute reflectance of a white film and its major variables. The K-M theory has been modified to allow for the practical variables that occur in bound systems. The problems left to be solved are those of the practical determination of absolute reflectance and film thickness.

The use of reference standards for the accurate determination of absolute reflectance depends on a knowledge of the precise optical conditions under which the references themselves have been calibrated, and also of the optics of the instruments in which they are subsequently used. Though such standards are necessary for maintaining constant working conditions on any one piece of equipment, they rarely give true absolute reflectances (e.g. to $\pm$ 0.002).

This difficulty has been overcome by adding another constant to equation (6), i.e. the factor necessary to convert accurate relative values of reflectance to absolute values. The equation becomes

$$R_M/A = (SX + M)/(SX + N) \ldots\ldots\ldots\ldots\ldots (7)$$

where R_M is the measured reflectance and A represents the 100 per cent reflectance reading on the reflectometer. The value of A is then found from analysis of the results. Once A is known, the standards used on the apparatus can be recalibrated.

A further problem that this approach resolves is the adjustment of results for the loss of intensity due to initial specular reflectance of the incident light beam at the air/paint surface. It is implied in equation (6) that there is unit light intensity incident on the scattering bulk of the film. The value of A determined from analysis of the results using equation (7) automatically contains the factor by which all the reflectances are reduced.

The initial specular surface reflectance can be treated in this way provided none of the reflected component is registered by the photodetector. A more complex correction is necessary for instruments in which the specular component is included in a measure of total reflectance. An independent measure of the specular component is then required.

The method outlined above for reducing relative reflectances to their absolute values by applying equation (7) can only be justified by examination of the final results. Its success relies on accurate determinations of relative reflectance and absolute film thickness. The former of these two can be attained by regular use of a reference standard. The latter, however, represents a major source of error in practical reflectance work.

Film thickness

In part I, the measurement of film thickness was determined using X-ray fluorescence from the titanium in the film. Since the mathematical analysis for finding the substrate reflectance is susceptible to errors in film thickness, this method of finding the thickness has been carefully scrutinised. The final determination of thickness requires a knowledge of the volume concentration of pigment within the film and this in turn depends on pigment and binder densities being known.

In the presentation of the results in part I, it has been tacitly assumed that the pigment is 100 per cent TiO_2. This stems from a natural inclination to measure pigmentary properties per unit quantity of purchased pigment. This assumption has been made in determining film thicknesses in part I. However, for fundamental work on the physical properties of TiO_2, more detail is necessary. Surface treatment of rutile pigments for their various applications reduces the TiO_2 content slightly and allowance must be made for this in the thickness determination. The TiO_2 content of the pigments studied in this project is 95 per cent. When this fact is taken into account and the thicknesses recalculated from the X-ray data, the nominal 10.0, 12.5 and 15.0 micron values become 10.5, 13.0 and 15.6 microns.

The constants r_1 and D

Equation (7) contains five unknowns other than the experimentally measured quantities R_M and X. Obviously, therefore, some of these must be found from other experimental work. The primary purpose of the current work is to study the variation of reflectance, R_M, with thickness, X, back-scattering coefficient, S, and substrate reflectance, r_2. The remaining constants, r_1 and D, needed to define M and N, have been obtained separately. The experimental techniques for finding these quantities are complex and for the purposes of this paper the results will be stated without a full description of their derivation.

The internal specular reflectance for diffuse light, r_1, is prone to variation owing to changes in gloss and also at higher pigment concentrations owing to optical interference effects in the clear surface layer of the film. However, a value of 0.55 for r_1 has been found to apply fairly consistently for volume concentrations below about 25 per cent. Although some of the concentrations of roller coatings in this work exceed 30 per cent, it has been assumed that the value of 0.55 applies in all cases.

Experimental determinations of D have indicated that it is independent of pigment concentration, a value of 0.50 having been found for systems pigmented with rutile.

The experimental data

Two sets of data have been presented in part I of this paper. For the purposes of testing the theoretical expression, only the set containing results for two pigments over six different substrates will be analysed. These are shown in part I, Table 4, in the form of the Harrison reflectance reading at 10, 12.5 and 15 microns nominal film thickness for each system studied.

Analysis of results

Equation (7) can be rearranged to give the following expression:

$$1/(A/R_M - 1) = (SX + M)/(N - M) \quad \text{..........(8)}$$

From equation (6) it can be shown that the quantity $(N - M)$ is given by

$$N - M = \frac{1 + (1 - r_1)\,D}{(1 - r_1)} \quad \text{................(9)}$$

Thus $(N - M)$ is dependent on only r_1 and D and is constant for all the films considered. Using values of 0.55 and 0.50 for r_1 and D gives $(N - M) = 2.72$. Equation (8) can now be written as

$$1/(A/R_M - 1) = SX/2.72 + M/2.72 \quad \text{..........(10)}$$

This is the basic equation used to analyse the experimental results. A value of A is found for each paint over the six substrates by minimising the spread of slopes in the six plots of equation (10). This procedure is repeated for the eight paints considered (two pigments at four concentrations) and a final average value is obtained for A. The method gave a value of 627 for the results in this paper.

The Harrison reflectances can now be reduced to their absolute values. These are listed in Table 1. They represent the reflectances for unit incident light intensity just inside the air/resin boundary.

Average values of the eight scattering coefficients, together with averages for the values of the constant M for the six substrates, can now be found either graphically or by calculation. For the initial analysis it was assumed that any one substrate has the same reflectance for all films applied to it. This assumption is not strictly correct, since it will be shown later how the substrate reflectance depends on pigment concentration. However, the following analysis shows that the variations in overall reflectance caused by this effect are small.

Table 1

Absolute values of Harrison reflectances

Pigment	Pigment Volume Concentration	Film thickness	Substrate					
			Sized			Unsized		
			S2	S3	S4	S2	S3	S4
P2	C1	F1	0.697	0.764	0.671	0.687	0.727	0.667
		F2	0.730	0.788	0.715	0.729	0.762	0.715
		F3	0.761	0.810	0.751	0.758	0.788	0.748
	C2	F1	0.722	0.785	0.699	0.710	0.756	0.707
		F2	0.761	0.810	0.748	0.751	0.788	0.758
		F3	0.789	0.828	0.778	0.783	0.812	0.789
	C3	F1	0.721	0.780	0.702	0.702	0.754	0.702
		F2	0.762	0.810	0.745	0.748	0.788	0.746
		F3	0.793	0.829	0.777	0.781	0.810	0.777
	C4	F1	0.719	0.785	0.702	0.707	0.754	0.692
		F2	0.762	0.810	0.746	0.753	0.788	0.740
		F3	0.793	0.828	0.777	0.785	0.810	0.774
P3	C1	F1	0.702	0.764	0.684	0.686	0.732	0.670
		F2	0.743	0.791	0.724	0.729	0.767	0.721
		F3	0.770	0.810	0.758	0.758	0.793	0.758
	C2	F1	0.719	0.781	0.708	0.713	0.750	0.707
		F2	0.762	0.805	0.750	0.750	0.785	0.746
		F3	0.786	0.825	0.781	0.781	0.809	0.777
	C3	F1	0.721	0.774	0.700	0.707	0.748	0.697
		F2	0.758	0.801	0.743	0.746	0.783	0.742
		F3	0.789	0.821	0.775	0.777	0.807	0.769
	C4	F1	0.703	0.770	0.683	0.700	0.743	0.686
		F2	0.742	0.799	0.727	0.740	0.774	0.735
		F3	0.770	0.818	0.761	0.770	0.797	0.769

Knowing the six values of M, each reflectance in Table 1 can be converted to a value of S using the following expression derived from equation (6):

$$S = \frac{1}{X}\left[\frac{2.72\,R}{1-R} - M\right] \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

These results are shown in Table 2. For each of four concentrations of two pigments, 18 values of S are given. The variance of each set of 18 can be found and the eight variances so obtained can be pooled to give a final standard deviation for the complete set. This standard deviation can be converted to an equivalent Harrison reading deviation using average values for S, X and M. The value obtained is 2.1 Harrison units, which compares very favourably with the error of 1.5 units determined from the residual variance of the analysis in part I.

Table 2

Values of S obtained from Table 1

Pigment	Pigment Volume Concentration	Film thickness	Substrate						Average	Standard deviation
			Sized			Unsized				
			S2	S3	S4	S2	S3	S4		
P2	C1	F1	0.527	0.521	0.518	0.534	0.507	0.515	0.519	0.008
		F2	0.510	0.519	0.512	0.531	0.521	0.519		
		F3	0.507	0.529	0.517	0.519	0.522	0.514		
	C2	F1	0.606	0.627	0.589	0.598	0.619	0.621	0.617	0.017
		F2	0.608	0.635	0.610	0.601	0.627	0.650		
		F3	0.606	0.623	0.603	0.603	0.627	0.650		
	C3	F1	0.601	0.601	0.598	0.574	0.612	0.607	0.608	0.015
		F2	0.614	0.635	0.600	0.590	0.627	0.612		
		F3	0.619	0.632	0.597	0.598	0.619	0.603		
	C4	F1	0.596	0.627	0.599	0.588	0.612	0.580	0.608	0.015
		F2	0.614	0.635	0.605	0.606	0.627	0.591		
		F3	0.619	0.623	0.597	0.609	0.619	0.592		
P3	C1	F1	0.541	0.521	0.538	0.529	0.524	0.523	0.534	0.008
		F2	0.548	0.534	0.538	0.531	0.539	0.536		
		F3	0.537	0.529	0.536	0.519	0.541	0.541		
	C2	F1	0.596	0.610	0.618	0.608	0.592	0.621	0.607	0.009
		F2	0.614	0.608	0.615	0.595	0.612	0.617		
		F3	0.594	0.604	0.614	0.598	0.611	0.603		
	C3	F1	0.601	0.568	0.594	0.588	0.585	0.593	0.591	0.010
		F2	0.597	0.582	0.594	0.585	0.605	0.596		
		F3	0.606	0.587	0.592	0.581	0.604	0.576		
	C4	F1	0.546	0.552	0.546	0.569	0.566	0.563	0.559	0.012
		F2	0.543	0.574	0.547	0.564	0.564	0.577		
		F3	0.537	0.570	0.545	0.559	0.561	0.576		

Thus, application of equation (6), and the assumption that the reflectance of any substrate is independent of the applied paint, have not introduced any serious errors into the calculations.

The values obtained for M, and hence substrate reflectance, r_2, can now be analysed in more detail.

The substrate reflectances

A comprehensive analysis of the relationship between unsized and sized substrate reflectance can now be attempted. The final equations will be used to illustrate why the initial assumption about the constancy of M was valid for the range of pigment concentrations used in this work.

The values of M, together with the corresponding substrate reflectances, are listed in Table 3.

Some initial observations can be made. It is immediately apparent that sizing increases the substrate reflectance, though the magnitude of the effect differs considerably from surface to surface. It is considered that this is due to the degree of smoothness of the metal surface. The burnished steel and Bright Hitop steel have similar optical constants and should theoretically have the same substrate reflectance when both are optically flat. However, it was visually noticeable that the burnished steel had a much rougher finish than the Bright Hitop, which in turn did not exhibit the "polish" of the electroplate. It would seem reasonable to suppose, therefore, that the reduced

Table 3
Relation of M and substrate reflectances

Substrate	M	r_2
S4—Burnished steel—unsized	0.05	0.36
S2—Bright Hitop —unsized	0.40	0.47
S3—Electrolytic tinplate—unsized ..	1.95	0.71
S4 Sized	0.14	0.39
S2 ,, ...	0.74	0.55
S3 ,, ...	3.35	0.79

substrate reflectance and the small sizing effect on the burnished steel are caused by surface roughness. Caution must be exercised, however, in attempting to correlate a visual estimate of "polish" with a measured diffuse light reflectance. Another point worth noting from the values of M given in Table 3 is that at high values of r_2, M increases very rapidly for small changes in r_2. Natural variations in r_2 for the electroplate, owing to production variables and surface texture, can thus lead to marked variations in final reflectance of applied paint films.

The effect of sizing on metal substrate reflectance

The theoretical approach

The equations needed to calculate the substrate reflectances from the optical constants of the media involved have been given in a previous paper[2]. They are complex and are repeated in an appendix to this paper. However, although they are necessary for a comparison of theory and experiment in this work, it will be shown later how simpler, approximate, expressions can be used for practical application of the reflectance equations given herein.

The sized metal system is shown schematically in Fig. 1, where the boundary reflectances for diffuse light have been denoted by R, with subscripts p (paint),

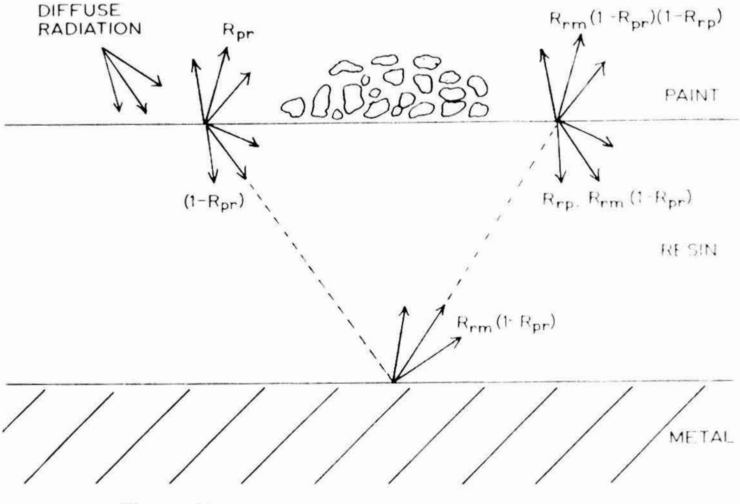

Fig. 1. The reflectances at a resin-metal substrate

r (resin) and *m* (metal) indicating the media involved and the direction of the radiation. The reflectance responsible for the enhancement of overall reflectance due to introducing the sizing layer is R_{pr}, the reflectance of diffuse light at the paint/resin boundary. It has been shown previously[2] that the presence of pigment in a resin increases its effective refractive index for boundary reflectances. The paint has, therefore, a higher refractive index than the clear resin and some of the diffuse light incident from the paint on to the boundary between the two experiences total internal reflection. The relationship between diffuse light reflectance and relative refractive index is shown in Fig. 2. Two curves corresponding to the two directions of incidence are given, the equivalent quantities from Fig. 1 being marked on each.

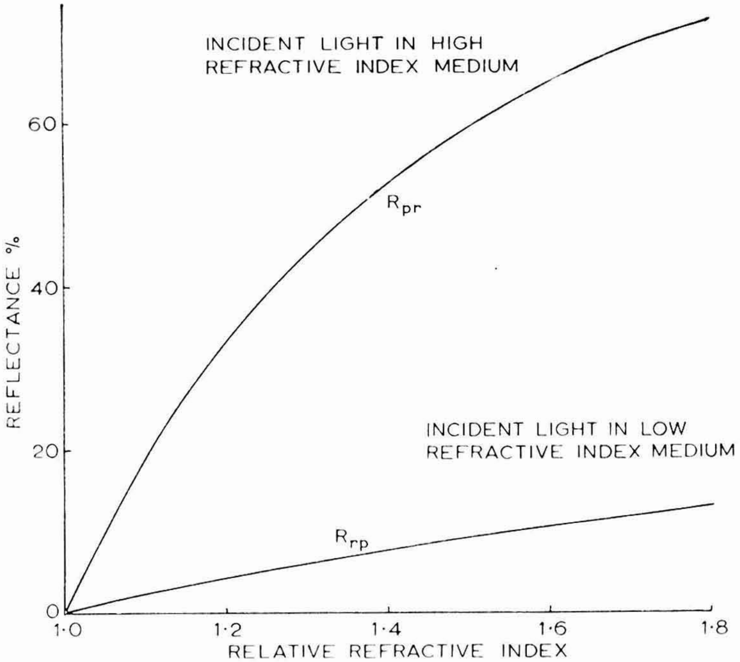

Fig. 2. Reflectance of diffuse light at a boundary between non-absorbing media

Two points should be noted from the figure. First, the reflectance for radiation incident on the high refractive index side of the boundary is large for quite small refractive index differences. Secondly, the reflection for radiation incident in the low refractive index medium is considerably lower than for the other direction. It will be shown later that this much lower reflectance can be ignored in the final, simplified approximate equations.

The application of the full equations in the appendix requires refractive index data for the media involved. The values that have been used are

clear resin	1.50
steel	2.50-3.40*i*
tin	1.07-4.25*i*

There is some doubt about the accuracy of these figures. The steel values are subject to error since they depend on the composition of the steel. The tin values are those that apply at a wavelength of 550nm. However, they vary with wavelength to some extent and this may well introduce an error, since no attempt has been made to average data over the wavelength response characteristics of the Harrison reflectometer.

An effective refractive index for the paint was found by applying the full calculations to the paint/resin/tin system and varying the paint refractive index until the theoretical substrate reflectance agreed with the experimental value of 0.79. The tin substrate was expected to correspond most closely to the theory, because of its superior surface finish. It was also the substrate for which r_2 could be most accurately determined, the M value being much more sensitive to changes in r_2 at high values of r_2. This procedure gave a value of 1.66 for the refractive index of the paint. This will be discussed in more detail shortly.

Application of the full equations in the appendix gave boundary reflectances for incident diffuse light as shown in Table 4 (experimental values for the Hitop steel and tin are shown in brackets).

Table 4

Boundary reflectances for incident diffuse light

Paint/steel	0.452	(0.47)
Resin/steel	0.475	—
Paint/resin/steel ..	0.575	(0.55)
Paint/tin	0.729	(0.71)
Resin/tin	0.743	—
Paint/resin/tin ..	0.791	(≡ 0.790)

The comparison between theory and experiment is very good, and justifies the assumptions made initially in the analysis of the results.

The resin/metal boundary does not occur separately without the paint/resin boundary, but the calculated results have been included in the list. This is to illustrate the fact that merely reducing the refractive index of the medium adjacent to a metal increases the reflectance at the boundary between the two. Thus the resin/metal boundary would be expected to reflect more than the paint/metal boundary. This effect certainly contributes to the overall enhancement of reflectance produced by interposing the clear layer between paint and metal. However, the contribution represents only about 25 per cent of the total effect.

Approximate equation

The equations in the appendix are bulky and require computer facilities for their application. Fortunately, some very simple approximate equations can be substituted in their place without sacrificing accuracy to any great extent.

A major assumption in this approximation is that the radiation remains diffuse in nature after boundary reflection and transmissions. From Fig. 1, the total boundary reflectance of the system can be achieved by summing the successive reflected components.

Total boundary reflectance:

$$r_2 = R_{pr} + (1-R_{rp}) \,.\, R_{rm} \,.\, (1-R_{pr}) + (1-R_{rp}) \,.\, R_{rp} \,.\, R_{rm}^2 \,.\, (1-R_{pr}) + \text{-----}$$

$$= R_{pr} + (1-R_{rp})\,(1-R_{pr}) \,.\, R_{rm}\,(1 + R_{rp} \,.\, R_{rm} + \text{----})$$

i.e.
$$r_2 = R_{pr} + \frac{(1-R_{rp})\,(1-R_{pr}) \,.\, R_{rm}}{(1-R_{rp} \,.\, R_{rm})} \quad \text{........................}(12)$$

It was shown in the previous section that the paint refractive index is effectively 1.66. From Fig. 2 it can be seen that the values of R_{pr} and R_{rp}, corresponding to a relative refractive index of 1.66/1.50 (= 1.107) at the paint/resin boundary, are 0.21 and 0.03 respectively.

Since R_{rp} is so small, the factor

$$\frac{(1-R_{rp})}{(1-R_{rp} \,.\, R_{rm})}$$

in equation (12) can be taken as unity. The error that arises from this approximation decreases as the reflectance at the metal increases. This is a welcome effect since the overall reflectance of the system becomes more sensitive to changes in r_2 as the value of r_2 increases. The substrate reflectance can now be written as

$$r_2 = R_{pr} + (1-R_{pr}) \,.\, R_{rm} \quad \text{..................}(13)$$

This now represents the main expression for r_2. The value of R_{pr} is related to refractive index in Fig. 2. The quantity R_{rm} still remains a computational problem. As a further simplification, it is suggested that R_{rm}, the metallic reflectance of diffuse light, be replaced by the reflectance value for a parallel beam of light at normal incidence. This quantity can be denoted by P_{rm}. If the metal refractive index is given by

$$\bar{n} = n_m - ik,$$

then P_{rm} is given by

$$P_{rm} = \frac{(n_m - n)^2 + k^2}{(n_m + n)^2 + k^2} \quad \text{..................}(14)$$

where n is the refractive index of the non-absorbing medium adjacent to the metal. Table 5 shows the values of P_{rm} and the fully computed values of R_{rm} for the paint/tin and paint/steel boundaries.

Table 5

Values of P_{rm} and R_{rm} for paint/tin and paint/steel boundaries

System	n_m	k	n	P_{rm}	R_{rm}
Paint/tin ..	1.07	4.25	1.66	0.722	0.729
Paint/steel ..	2.50	3.40	1.66	0.425	0.452

Once again the error involved in this approximation decreases as R_{rm}, and hence r_2, increases.

A full comparison can now be made between the approximate approach using equations (13) and (14), the full calculation given in the appendix and the experimental results. These are summarised in Table 6.

Table 6

Comparison of experimental results with exact and approximate calculations

Substrate system	Substrate reflectance		
	Experimental	Exact calculation	Approximate calculation
Paint/steel	0.47	0.452	0.425
Paint/resin/steel ..	0.55	0.575	0.568
Paint/tin	0.71	0.729	0.722
Paint/resin/tin ..	0.79	0.791	0.793

The difference between the experimental and approximate calculation values for the paint/steel substrate appears excessive. In fact, by substitution of these values back into the reflectance equation (6), it can be shown that this represents a difference of 2-3 Harrison reflectance units, little more than the expected error.

The refractive index of the paint

The analysis of the results has produced a value of 1.66 for the paint. This assumes a resin refractive index of 1.50. Since it has been assumed that all the paints involved in this work have the same refractive index, the value of 1.66 represents an average value for the two pigments at the four concentrations considered. Two other sources of experimental measurements of paint refractive index are known. Kawabata[5] measured the gloss values of the substrate surface of free paint films and converted these into effective refractive indices. Taking the average of his results at the four pigment concentrations given in this paper gives a value of 1.66. One of the authors used an entirely different approach[6] to measuring the refractive index and found an average value of 1.65.

Hence the value that has been found in the analysis of the roller coating reflectances agrees very well with those obtained by other methods. Some variation is to be expected since precise medium refractive indices have not been given.

The effect of varying the refractive index of the paint can be assessed by applying the approximate equation given previously. Kawabata's results implied refractive indices of 1.61, 1.64, 1.67 and 1.70 at the pigment concentrations used in this paper. The calculations show that, for the sized substrates, the total substrate reflectance increases with paint refractive index. For the tin substrate, this effect introduces a standard deviation of 2.3 in reflectance readings. For the steel, the standard deviation is 1.6.

The reverse occurs on the unsized metal surfaces. Increasing the paint refractive index slightly decreases the final opacity. The standard deviations in Harrison readings expected for this effect with tin and steel are 0.6 and 0.3.

Thus the effects of the varying paint refractive index on the results in this paper are small. The calculations confirm the earlier experimental conclusion that the substrate reflectance can be taken as constant for the range of pigment volume concentrations used in this paper (nominally 18.5 per cent to 31.5 per cent). A much wider range would be necessary to illustrate experimentally the effects of pigment concentration on substrate reflectance.

The statistically significant interactions

The significant factors controlling the reflectance of roller coatings were obtained by an analysis of variance in part I of the paper. A comparison can now be made between these results and the equations given in part II. They will be briefly considered individually in order of decreasing variance ratio (part I, Fig. 6).

Film thickness

Equation (6) covers this factor.

Substrate

Equation (14) shows that the substrate reflectances are functions of the optical constants of the individual metals.

Pigment concentration

This appears as a variation in the scattering coefficient used in equation (6). This has not been considered in part II.

Sizing of the substrate

Equation (13) covers this effect.

Sizing × substrate

This interaction is due to the effect of sizing being different on different metal substrates. Although this is expected theoretically, the main source of this interaction is most probably the variation in smoothness of the metals, and the consequent lack of effect of sizing on the rougher surfaces.

Substrate × film thickness

This interaction is a direct consequence of the form of equation (6). It is evident that the substrate has less effect as the quantity SX increases.

Pigment; pigment × concentration

These give variations in scattering coefficient and have not been considered.

Pigment concentration × substrate

This is a small effect owing to variation of the paint refractive index with changing concentration.

Pigment × concentration × sizing

This is slightly obscure. It could represent a variation of refractive index of the paint that is a function of pigment dispersion. It could be a measure of the homogeneity of the paint and its influence on the total internal reflection properties at the paint/resin boundary. However, if this were the case then a significant concentration × sizing interaction would also be expected.

Summary of equations

The reflectance of a white roller coating is given by :

$$R = \frac{SX + M}{SX + N}$$

where S = back-scattering coefficient of the pigment

X = film thickness

and M and N are defined by the following expressions:

$$M = \frac{r_2 - D\,(1 - r_2)}{(1 - r_2)}$$

$$N = \frac{(1 - r_1 r_2)}{(1 - r_1)\,(1 - r_2)}$$

where r_1 = the internal paint/air boundary reflectance for diffuse light

r_2 = the paint/substrate reflectance for diffuse light

D = a diffusion constant.

Values of 0.55 and 0.50 have been successfully used for r_1 and D. A simple expression for r_2 can be used, i.e.

$$r_2 = R_{pr} + (1 - R_{pr}) \, . \, R_{rm}$$

where R_{pr} = the boundary reflectance at the paint/resin boundary.

Values of R_{pr} can be obtained from relative refractive index (paint refractive index/resin refractive index) using Fig. 2. The reflectance of diffuse light at the dielectric/metal boundary, R_{rm}, can be approximately obtained using the formula for a parallel beam at normal incidence, i.e.

$$R_{rm} \equiv P_{rm} = \frac{(n_m - n_d)^2 + k^2}{(n_m + n_d)^2 + k^2}$$

where $n_m - ik$ = refractive index of the metal

n_d = refractive index of the medium adjacent to the metal.

Comparison between the full theory and the experimental results

A comparison can now be made between the reflectances calculated from the equations summarised above and the experimental values. In Figs. 3 to 6, the solid lines represent the theoretical prediction of the Harrison readings for pigment, $P3$, the bars being the experimental values for the Hitop steel and tin substrates. The error shown is ±1.5 points, i.e. one standard deviation.

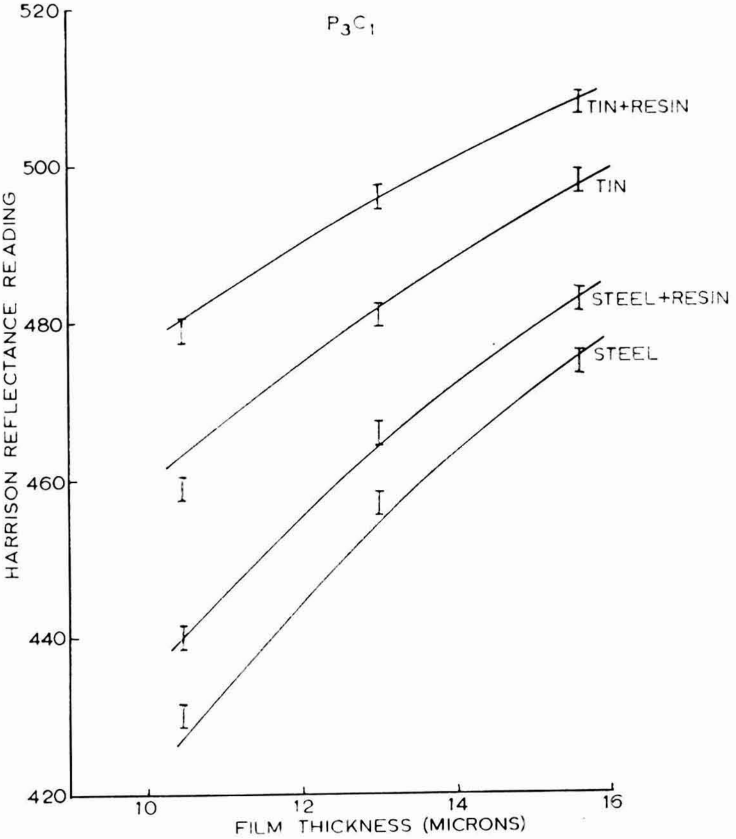

Fig. 3. Predicted and measured values of Harrison reflectance v film thickness

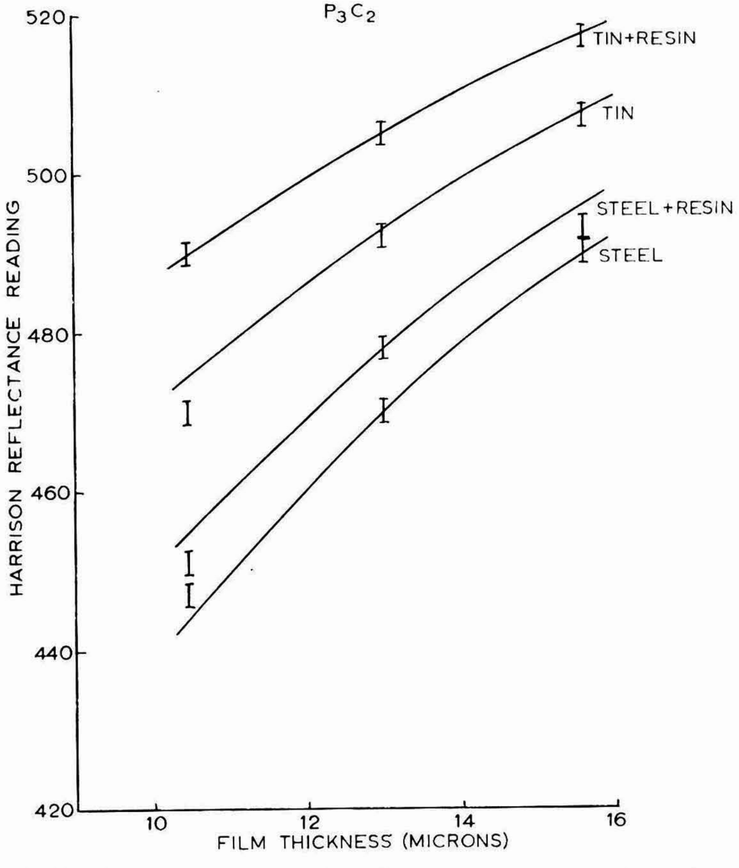

Fig. 4. Predicted and measured values of Harrison reflectance v film thickness

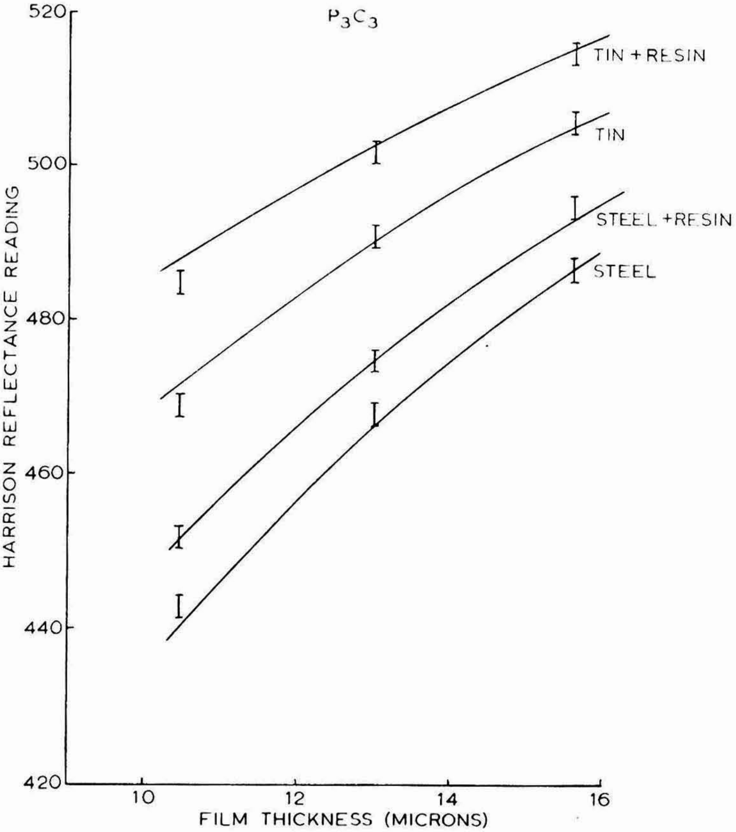

Fig. 5. Predicted and measured values of Harrison reflectance v film thickness

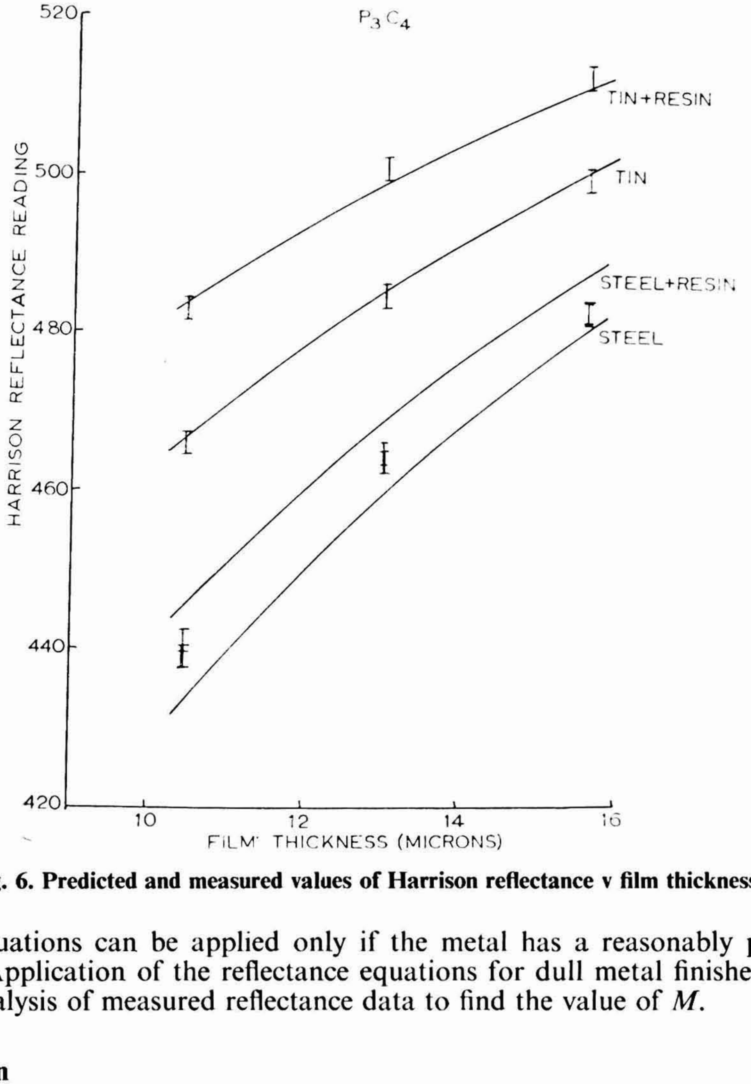

Fig. 6. Predicted and measured values of Harrison reflectance v film thickness

The equations can be applied only if the metal has a reasonably polished surface. Application of the reflectance equations for dull metal finishes necessitates analysis of measured reflectance data to find the value of M.

Conclusion

Soundly based approximate expressions have been derived theoretically and applied successfully to the experimental results. It has been shown quantitatively how the reflectance of white roller coatings depends on film thickness and substrate reflectance. Expressions are given for obtaining the substrate reflectance from the fundamental optical constants of the media involved.

It is evident from the results that the surface finish of the metal substrate has an important bearing on its reflectance properties and on the magnitude of the reflectance enhancement produced by sizing.

The practical equations given in the paper are very simple in form and easy to apply. They are not restricted to roller coatings and can be applied with similar success to thicker white films.

Acknowledgments

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Appendix

Calculation of the reflectance of a resin/metal substrate for diffuse incident light

Fig. 7 shows the multiple reflectances that occur in the system for light incident at angle θ. The refractive indices of the system are denoted by n_1, for the paint, n_2 for the resin, and n_3-ik for the metal.

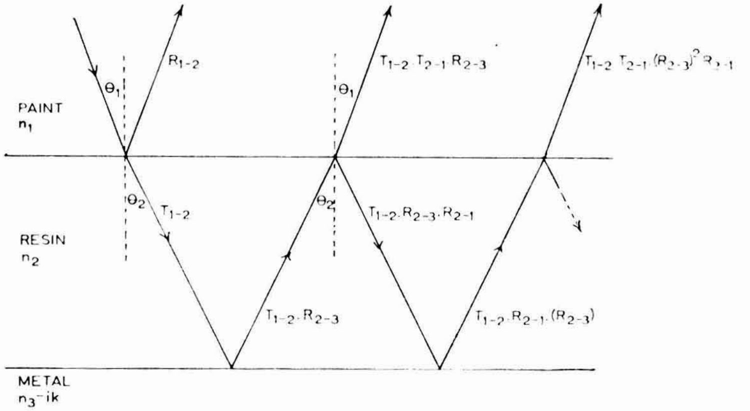

Fig. 7. Multiple reflectance at the substrate of a paint-resin-metal system

The total reflectance at incident angle θ_1 is given by

$$R_\theta = R_{1-2} + \frac{T_{1-2} \cdot T_{2-1} \cdot R_{2-3}}{[1 - R_{2-1} \cdot R_{2-3}]} \quad \dots\dots\dots\dots\dots\dots (1)$$

where R and T represent reflectance and transmittance and the subscripts refer to the media involved and the direction of incidence. R_θ consists of two parts corresponding to the two planes of polarisation into which the incident diffuse light can be equally divided. The total reflectance for diffuse light is then given by

$$R_T = \int_0^{\pi/2} \frac{1}{2}\,(R_\theta^s + R_\theta^p) \,.\, \sin\theta \cos\theta \, d\theta \quad \dots\dots\dots\dots (2)$$

where the superscripts s and p refer to the two states of polarisation.

The component reflectances and transmittances to be substituted into equation (1) are as follows:

Fresnel's equations can be applied directly to the boundary between media 1 and 2 to give

$$R^s_{1-2} = R^s_{2-1} = \frac{\sin^2(\theta_1 - \theta_2)}{\sin^2(\theta_1 + \theta_2)}$$

$$R^p_{1-2} = R^p_{2-1} = \frac{\tan^2(\theta_1 - \theta_2)}{\tan^2(\theta_1 + \theta_2)}$$

where $n_1 \sin \theta_1 = n_2 \sin \theta_2$.

Also
$$T^s_{1-2} = \frac{4 \sin^2 \theta_2 \, . \, \cos^2 \theta_1}{\sin^2(\theta_1 + \theta_2)}$$

$$T^p_{1-2} = \frac{4 \sin^2 \theta_2 \, . \, \cos^2 \theta_1}{\sin^2(\theta_1 + \theta_2) \, . \, \cos^2(\theta_1 - \theta_2)}$$

$$T^s_{2-1} = \frac{4 \sin^2 \theta_1 \, . \, \cos^2 \theta_2}{\sin^2(\theta_1 + \theta_2)}$$

$$T^p_{2-1} = \frac{4 \sin^2 \theta_1 \, . \, \cos^2 \theta_2}{\sin^2(\theta_1 + \theta_2) \, . \, \cos^2(\theta_2 - \theta_1)}$$

The reflectance at the metal surface is complex.

$$R^s_{2-3} = \frac{(n_2 \cos \theta_2 - u_3)^2 + v_3^2}{(n_2 \cos \theta_2 + u_3)^2 + v_3^2}$$

$$R^p_{2-3} = \frac{[(n_3^2 - k^2) \cos \theta_2 - n_2 u_3]^2 + [2 n_3 k \cos \theta_2 - n_2 v_3]^2}{[(n_3^2 - k^2) \cos \theta_2 + n_2 u_3]^2 + [2 n_3 k \cos \theta_2 + n_2 v_3]^2}$$

where

$$2u_3^2 = [n_3^2 - k^2 - n_2^2 \sin^2 \theta_2] + [(n_3^2 - k^2 - n_2^2 \sin^2 \theta_2)^2 + 4 n_3^2 k^2]^{0.5}$$

$$2v_3^2 = -[n_3^2 - k^2 - n_2^2 \sin^2 \theta_2] + [(n_3^2 - k^2 - n_2^2 \sin^2 \theta_2)^2 + 4 n_3^2 k^2]^{0.5}$$

If $\frac{n_1}{n_2} \sin \theta_1 \geqslant 1.0$, then $R^s_{1-2} = R^p_{1-2} = 1.0$ and $T^s_{1-2} = T^p_{1-2} = 0$.

Discussion at the Torquay Conference

Dr R. Bult (Chairman), referring to the effect of sizing on the substrate, said that a reflective surface would tend to be more uniform, and thus the thin layer of size would also tend to have a uniform surface. If the surface was rough, the peaks of the metal would tend to penetrate the thin resin film. Was not this an explanation for some of the anomalous results obtained?

Mr D. F. Tunstall agreed that this might be the case. Also, the interface between the paint and the resin would not be flat in such a case, and this would make the system more complex. A system of this complexity could not be treated on a macroplanar scale, which would invalidate many of the results, and thus explain some of those that were anomalous.

Mr P. Fink-Jensen said that a diffusion coefficient had been introduced into the calculations. It seemed from the mathematics that this was unnecessary, as the use of a modified reflectance would have served the same purpose. What particular theoretical reason did the author have for introducing the diffusion coefficient? Also, the use of the Saunderson correction had been referred to. In practice, these corrections seldom applied.

Mr Tunstall replied that the diffusion coefficient had been introduced to enable a true value of reflectance from the substrate to be calculated. Once this was known, it was easier to examine the effect of other factors such as pigment size, PVC, etc. Although the use of a modified reflectance would have solved the immediate problem in the mathematics, it would have been of no assistance in such later calculations. With regard to Saunderson's work, later work by Bridgeman had confirmed his value of the correction factor. Mr Tunstall himself had carried out similar work and come to a similar result. The difficulty was that the mathematics, while correct, was incorrectly applied—the factor was a mathematical artifice rather than a practical quantity.

Dr F. Vial pointed out that Kubelka-Munk scattering coefficients of the paint for the pigments at various PVC'S were quoted for metallic substrates. Had these coefficients been calculated on black substrates?

Mr Tunstall said that these values had not been determined separately on black substrates, but the estimated average values found for the various metal substrates had been used and shown to give the right answer. Although this might seem overconfident, it had been felt valid. Variations in reflectance of films on different black substrates were trivial compared with those on white.

Mr W. W. Gillison asked if the addition of optical brighteners to films of the type under discussion would be expected to have a beneficial influence on reflectance.

Mr Tunstall replied that the only way that the reflectance of visible radiation would be altered was if the amount of optical brightener added was sufficient to alter the refractive index of the paint.

Mr Gillison said that he was involved in work on solar heat reflective camouflage pigments and was wondering if there was any modification to the white undercoat which would improve its reflectance, particularly to heat reflection.

Mr Tunstall replied that this was a rather different field; infra-red radiation was involved. Pigments were designed to produce optimum reflectance of visible wavelengths of light, and inevitably their reflectances of infra-red radiation were lower. Added to this, organic materials in the binder would absorb at certain infra-red wavelengths. Only a specific investigation into infra-red reflectance would produce the answers Mr Gillison required.

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Several factors affecting appearance and properties of thermosetting acrylic resin based enamels*

By J. R. Taylor and H. Foster

BP Chemicals International Limited, Sully, Penarth, Glamorgan CF6 2YU

Summary

The surface properties and appearance of paint films have been studied in relation to a number of factors including oven flow, mar resistance and weathering. Reflow of a paint film during a double stoving cycle is discussed and an attempt is made to explain certain anomalies in the behaviour of three-component films, by consideration of the rate of cure and of the mutual compatibility of the reactive components of the binder.

Oven flow is then examined, and a method is proposed of following viscosity changes during the baking cycle of a thermosetting resin film, by measuring the velocity of fall of a sphere embedded in it when held in a vertical plane. Graphs are constructed which illustrate the difference in viscosity changes between reflow and conventional acrylic/melamine blends.

The weathering properties of alkyd and acrylic/melamine metallic enamels are described, and the surface appearance of these films is examined using a Stereoscan electron microscope; the presence of micro-checking on the surface of the alkyd film is revealed as a possible explanation of the loss of gloss obtained.

A method of measuring mar resistance by examining the profile of a scratch on the surface of an enamel film is suggested to confirm the improvement in mar resistance conferred by the application of a wax polish to a TSA enamel film.

Thermal effects and the mechanical forces acting at the points of contact during marring are considered, and the resulting temperature rise produced by an indentor on a TSA enamel film is calculated and may have a significant effect on the mar resistance of films possessing a slight degree of thermoplasticity.

Keywords

Types and classes of coating
enamel

Binders—resins etc
acrylic resin
melamine resin

Properties, characteristics and conditions primarily associated with dried or cured films
mar resistance
oven reflow
weather resistance

Quelques facteurs influant l'apparence et les propriétés des feuils d'émaux acryliques thermodurcissables

Résumé

Les caractéristiques superficielles et l'apparence du feuil de peintures ont été étudiés par rapport à plusieurs facteurs y compris, l'écoulement à l'étuve, la résistance aux chocs et aux intempéries. On discute le reflux d'un feuil de peinture pendant un cycle d'étuvage doublé et l'on a essayé d'expliquer certaines irrégularités de comportement des feuils de peinture à trois composants en considérant le taux de durcissement et la compatabilité mutuelle des constituents réactifs du liant.

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*Presented at the Torquay Conference on 7 May 1971.

Ensuite on a examiné l'écoulement à l'étuve, et l'on a proposé une méthode, pour suivre les changements de viscosité pendant le cycle de cuisson d'un feuil de résine thermodurcissable, où il s'agit de mesurer la vitesse de descente d'une sphère enfoncée dans le feuil qui est retenu dans un plan vertical. On a construit des courbes qui démontrent les différences entre les changements de viscosité des mélanges acrylique-mélamine conventionels et ceux des mélanges acrylique-mélamine à refluer.

On décrit la résistance aux intempéries des émaux alkyde ou acrylique-mélamine aux pigments métalliques, et l'on a examiné la surface de ces feuils au moyens d'un microscope électronique Stéreoscan. Dans le cas du feuil de résine alkyde, la présence du microfaiençage sur la surface se révèle en tant qu'une explication éventuelle de la perte du brillant mise en évidence.

Une méthode pour mesurer la résistance aux chocs par l'examen du profil d'une égratignure sur la surface d'un feuil d'émail a été suggérée afin de confirmer l'amélioration de résistance aux chocs fournie par l'application d'une encaustique au feuil d'émail acrylique thermodurcissable.

On a considéré les effet thermiques ainsi que les forces mécaniques qui agissent aux points de contact pendant les chocs, et l'on a calculé la hausse de température produite dans un feuil d'émail acrylique thermodurcissable par un style, et elle pourrait exercer une influence importante sur la résistance aux chocs des feuils ayant un degré de thermoplasticité léger.

Aussehen und Eigenschaften Wärmehärtbarer Akrylharzemaillefilme Beeinflussende Faktoren

Zusammenfassung

Die Eigenschaften der Oberflächen und das Aussehen von Lackfilmen wurden im Bezug auf eine Anzahl von Faktoren, darunter Verlauf im Ofen, Kratzfestigkeit und Wetterfestigkeit untersucht. Der zweite Fluss eines Lackfilms, durch zweimalige Ofentrocknung veraulasst, wird besprochen, und es wird versucht, gewisse Anomalien im Verhalten von Dreikomponenten-Lackfilmen unter Berücksichtigung der Härtungsgeschwindigkeit und der gegenseitigen Verträglichkeit der reaktiven Komponenten des Bindemittels zu erklären.

Der Verlauf im Ofen wurde untersucht. Eine Methode wird vorgeschlagen, die Viskositätsveränderungen bei der Ofentrocknungsperiode eines wärmehärtenden Kunstharzfilms durch Messung der Geschwindigkeit einer in ihm eingebetteten Kugel zu verfolgen. Der Film wird dafür vertikal gehalten. Kurven wurden entwickelt. welche den Unterschied im Bezug auf Viskositätsveränderungen zwischen schwitzbaren, konventionellen Alkydharz-Melaminharz und Verschnitten illustrieren.

Die Wetterbeständigkeitseigenschaften von Alkydharz- und Akrylharz- Melaminharz Metallikemaillelacken werden bschrieben, und das Aussehen der Oberfläche der Filme unter Benutzung des Stereoscanelektronenmikroskopes untersucht. Die dabei gefundene Anwesenheit von Mikrohaarrissen an der Alkydharzfilmoberfläche wird als eine mögliche Erklärung für den Glanzverlust angenommen.

Eine Methode zur Messung der Kratzfestigkeit durch Prüfung des Profiles eines Kratzers in der Lackfilmoberfläche wird vorgeschlagen, um die Verbesserung der durch Auftragen von Wachspolitur auf einen TSA Emaillelackfilm hervorgerufene verbesserte Kratzfestigkeit zu bestätigen.

Thermische Effekte und die an den Kontaktpunkten beim Kratzen wirkenden mechanischen Kräfte werden in Betracht gezogen, und auch die durch einen Indentor auf einem TSA Emaillelackfilm erzeugte Temperaturerhöhung wurde berechnet; diese könnte eine bedeutsame Wirkung auf die Kratzfestigkeit solcher Filme ausüben, welche etwas thermoplastisch sind.

Ряд факторов влияющих на наружный вид и свойства термореактивных акриловых эмалиевых пленок

Резюме

Изучались поверхностные свойства и вид красочных пленок по отношению к некоторым факторам включая течение в печи, сопротивление к поверхностному повреждению и выветривание. Обсуждалось повторное течение красочной пленки в двойном печном цикле и была сделана попытка объяснить некоторые аномалии в поведении 3-ех компонентных пленок, путем анализа скорости сушки и взаимной совместимости реактивных составных элементов крепителя.

Затем рассматривалось течение в печи и был предложен метод наблюдения изменений в вязкости во время цикла сушки термореактивной смольной пленки, путем измерения скорости движения шара погруженного в нее в вертикальной плоскости. Получены кривые иллюстрирующие различия в изменении вязкости между смесями повторного течения и обычными акрило-меламиновыми смесями.

Описываются свойства выветривания алкидных и акрило-меламиновых металлических эмалей и изучается поверхностный вид этих пленок, применяя стерео-поисковый электронный микроскоп и наличие микротрещин на поверхности алкидной пленки является возможным объяснением наблюдаемой потери лоска.

Предложен метод измерения сопротивления к наружному повреждению или царапинам, путем анализа профиля царапины на поверхности эмалиевой пленки, для подтверждения повышения сопротивления против наружного повреждения применением восковой полировки на термореактивной акриловой эмалиевой пленке.

Изучаются термические эффекты и механические силы действующие на точках контакта во время нанесения повреждения или царапины и вычисляется повышение температуры в результате нанесения повреждения индентором на термореактивной эмалиевой пленке и это может иметь значительное влияние на сопротивление повреждению пленок обладающих незначительной степенью термопластичности.

Introduction

The surface appearance of any solid material is usually described in terms of a number of visual characteristics such as gloss, colour, texture, uniformity, presence of foreign matter, etc. In the case of surface coatings, these properties are influenced by various factors, including the pigments, resins, solvents and additives used, and by environmental effects resulting from weathering, heat, and abrasion. The measurement and evaluation of surfaces, and in particular paint film surfaces, is an extensive subject, and the authors have necessarily limited their approach to certain specific topics. Some of the more recent methods of surface evaluation include evaporative rate analysis[1], Stereoscan electron microscopy[2, 3, 4, 5], and surface texture measurements by a Talysurf[4] instrument. Surface and total film compositions have been studied by Johnson[6, 7] using an abrasion method followed by infra-red analysis of the sample removed. The authors attempt in this paper to outline certain important considerations which are necessary to obtain an ideal surface in a paint film under industrial conditions. Such an ideal surface would be free from irregularities or extraneous matter, and would possess suitable mar resistance, hardness, flexibility and durability in the environment for which it is intended.

The reflow technique[8, 9] has assisted the end user to obtain paint films which are virtually free from imperfections, at the same time controlling to some extent the gloss, texture and uniformity of the surface of an enamel film. The concept of reflow involves the reduction in viscosity of a paint film during the baking cycle. When using standard stoving techniques without reflow, enamels exhibiting good oven flow are still preferred, in order to obtain optimum gloss and levelling properties. As far as the authors are aware, there has been little work done towards the measurement of viscosity changes during a baking cycle of a thermosetting reflow film, due to the sophisticated apparatus that would be necessary. Data is available regarding the viscosity of liquids at different temperatures as measured by instruments such as the Weisenberg Rheogoniometer[10], but it is difficult to adapt this instrument to the measurement of viscosity changes in a thermosetting paint film.

In this paper the authors attempt to study some of the parameters which affect reflow, and later suggest a method of measuring the flow of paint films during a baking cycle. This method is then adapted to show the differences in flow between conventional thermosetting media and reflow thermosetting media. Other properties closely associated with surface properties of enamel films, such as weathering and mar resistance, are also discussed.

Reflow

In a previous paper[8] the authors have considered the parameters affecting reflow, and the concept of centre line average (CLA) height of irregularities has now been used to quantify a degree of reflow which would be acceptable in industry.

In the current work, the authors have considered a CLA height of 0.05 micrometers after reflow to be the maximum permitted surface irregularity for a high gloss finish. This method was preferred to the measurement of percentage gloss recovery, since it gave more consistent results and followed more closely the visual assessment of reflow.

Effect of pigment, acrylic resin and melamine resin in a thermosetting reflow enamel film

In the following work, an initial low temperature bake of 15 minutes with a panel temperature of 100°C was used, and a final bake of 17 minutes at 138°C. The two resins used in the reflow enamels were a hydroxylated acrylic resin, Epok D2106, and an isobutylated melamine formaldehyde resin, Epok U9195. The acrylic resin is supplied as a 60 per cent solution in a mixture of xylol and *n*-butanol, at a viscosity of approximately 25 Stokes at 25°C, and an acid value of less than 10mg KOH/g. The melamine resin is supplied at 65 per cent solids in *iso*butanol at a viscosity of approximately 25 Stokes at 25°C.

A 400 grade sandpaper was used with a mineral seal oil as lubricant. The results of numerous experiments in which pigment : binder ratio and acrylic : melamine ratios were varied are shown in Fig. 1. The pigment used was a surface treated titanium dioxide (Tioxide RCR2) which was dispersed in the medium using a high speed ball mill. The area shaded with diagonal lines denotes enamel films which have a CLA height greater than 0.05 micrometers on the sanded area after the final stoving schedule. Two peaks, *A* and *B*, deserve consideration. Peak *A* was seen to coincide with the maximum hardness and degree of cure when the acrylic/melamine ratio was varied, as seen in Fig. 2. Peak *B* coincided with an inflection in the viscosity curve obtained when the acrylic:melamine ratio was varied, as shown in Fig. 3. This could be attributed to the incompatibility of the acrylic and melamine resins in the region of acrylic:melamine 50:50—20:80. A further relationship was seen in Fig. 4, in which the gloss of a series of enamels at a fixed pigment:binder ratio was measured, varying again the acrylic:melamine ratio. This variation was carried out along a line XY drawn on the initial triangular co-ordinate diagram shown in Fig. 1.

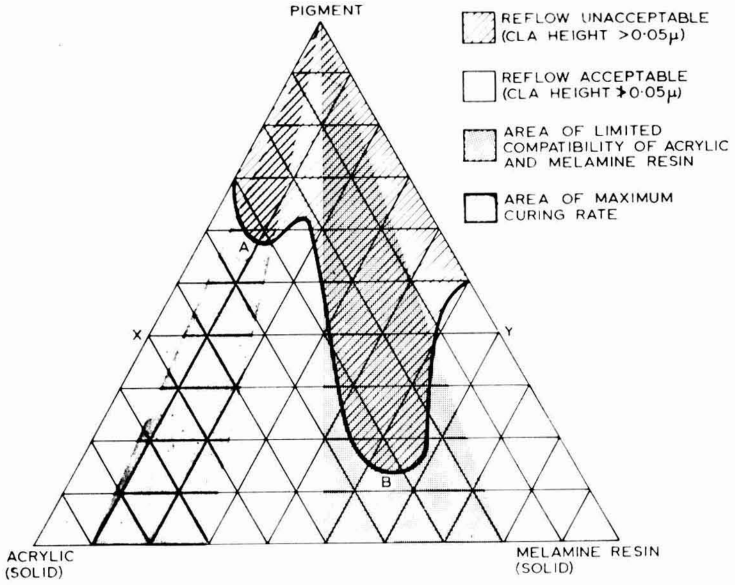


Fig. 1. Triangular co-ordinate diagram indicating limits of reflow in white acrylic:melamine enamel film

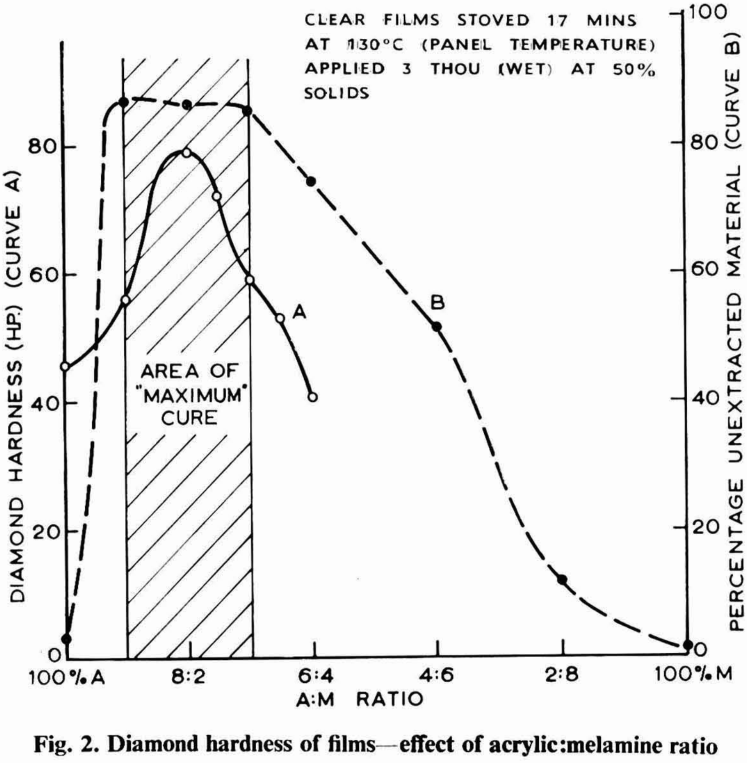


Fig. 2. Diamond hardness of films—effect of acrylic:melamine ratio

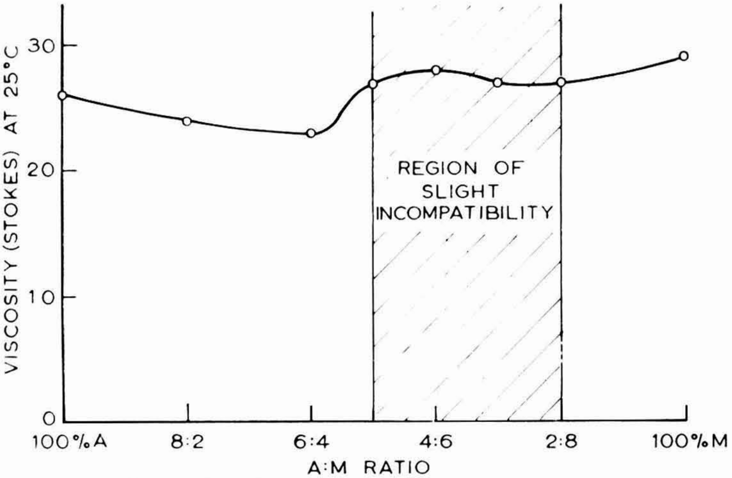


Fig. 3. Viscosity of acrylic:melamine resin blends

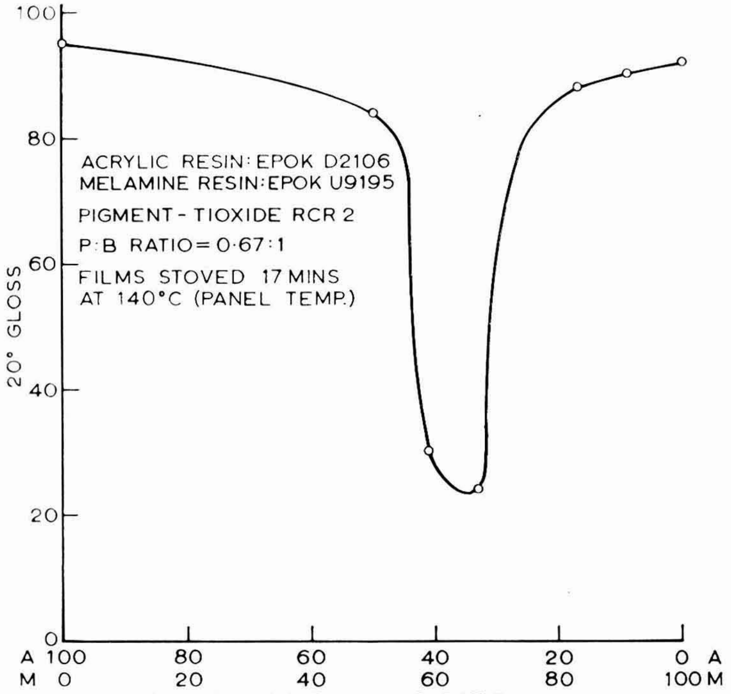


Fig. 4. 20° gloss of white enamels vs. acrylic:melamine ratio

Systems utilising more than one pigment

Further work was carried out using the optimum acrylic:melamine ratio of 7:3, which gave the best all-round properties.

Using this fixed acrylic:melamine ratio, it was possible to investigate the limits of satisfactory reflow using combinations of two pigments. Four particular pigmented systems of interest were:

Molybdate Red:Permanent Bordeaux FGR (Hoechst) (Fig. 5)
Alcoa 726:Cromophtal Blue A3R (Ciba-Geigy) (Fig. 6)
Alcoa 726:Degussa Carbon Black 1000G (Fig. 7)
Tioxide RCR2:Yellow Ochre MY42 (Fig. 8)

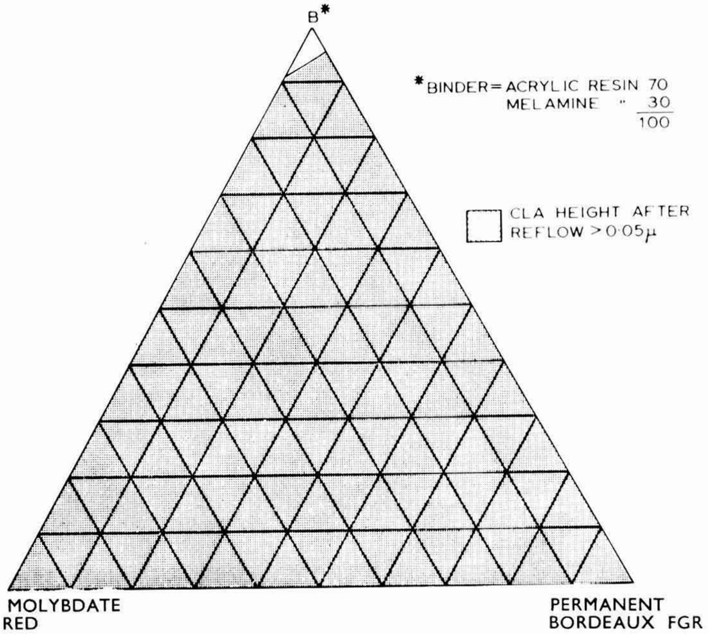


Fig. 5. Triangular co-ordinate diagram indicating limits of reflow in acrylic/melamine enamel films using Molybdate Red and Permanent Bordeaux FGR

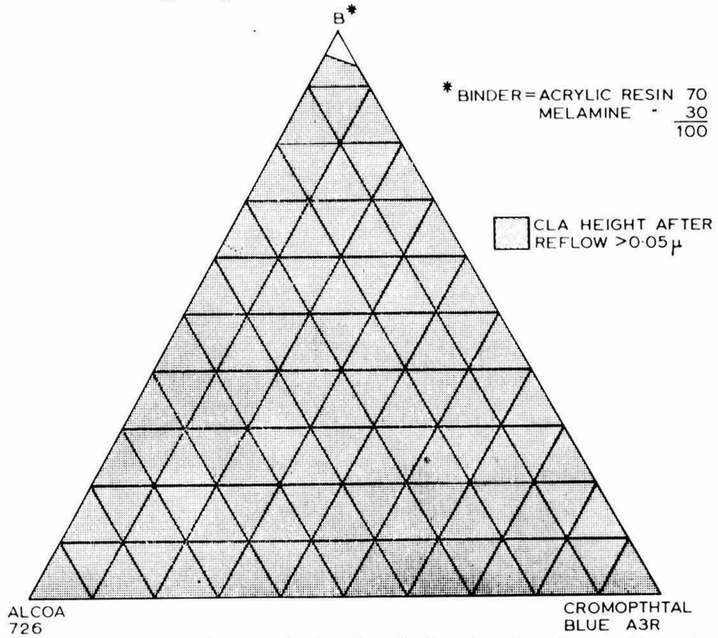


Fig. 6. Triangular co-ordinate diagram indicating limits of reflow in acrylic/melamine enamel films using Alcoa 726 and Cromophtal Blue A3R

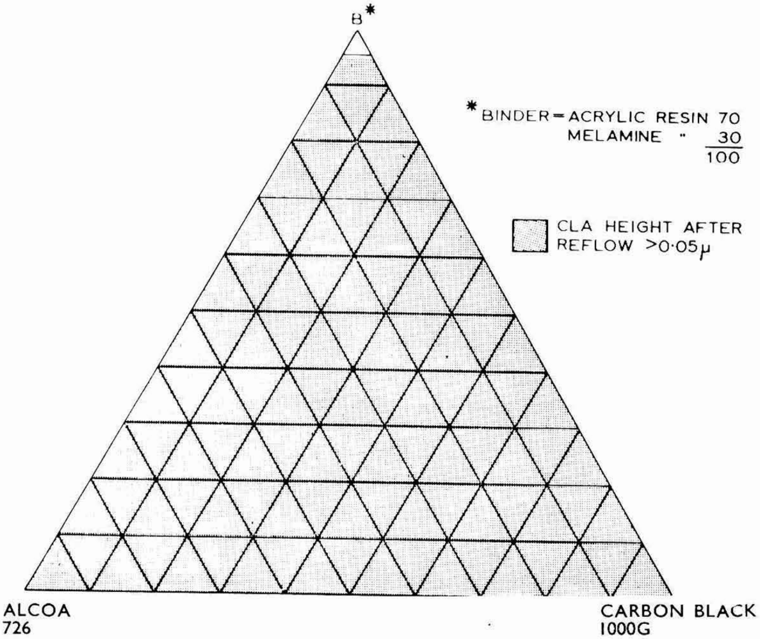


Fig. 7. Triangular co-ordinate diagram indicating limits of reflow in acrylic/melamine enamels using Alcoa 726 and Carbon Black 1000G

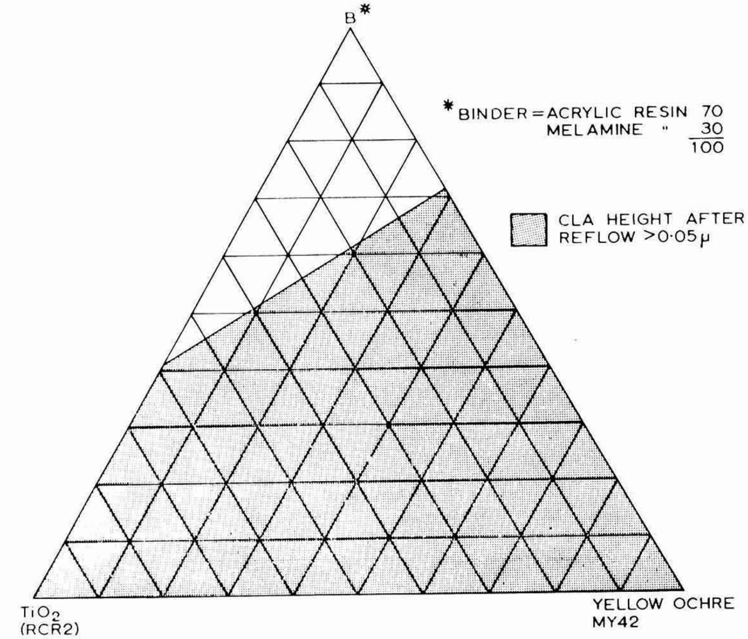


Fig. 8. Triangular co-ordinate diagram indicating limits of reflow in acrylic/melamine enamel films using titanium dioxide and Yellow Ochre MY42

The graphs indicate that the pigment has a profound effect upon the flow of the enamel films during the baking cycle. An attempt was made to establish a relationship between the oil absorption of the pigment and the maximum pigment concentration that gave acceptable reflow, but no correlation was evident. This was not unexpected in view of the number of other variables and mechanisms involved, such as the degree of dispersion of the pigment, its particle size distribution and the nature of its surface, the nature of the acrylic medium used, i.e. its pigment wetting properties compared with those of the linseed oil used in the determination of oil absorption, the stability of the dispersion, and deviations from Newtonian flow due to thixotropy, dilatency and pseudo-plasticity[11].

Rheological aspects of reflow and oven flow

During a stoving process, changes in temperature and viscosity occur in a paint film. With thermosetting films, the relationship is more complex than that for thermoplastic films, because of the cross-linking reaction[13]. A paint film will reflow during the high temperature bake, provided such factors as resin reactivity, intrinsic viscosity, oven temperature and efficiency, and pigmentation are carefully controlled. If the cross-linking reaction in a thermosetting system is very fast, there will be little or no opportunity for reflow to take place.

The authors have attempted to measure the apparent viscosities of a number of clear thermosetting resin films using a technique adapted from the falling sphere method of measuring the viscosity of a liquid. A small steel sphere (diameter 1.6mm) was embedded in a film of known thickness applied to a glass panel which was subsequently held in a vertical plane. In view of the fact that the sphere was not completely immersed in the film, it was necessary to establish a relationship between the apparent viscosity of the film and the velocity of the sphere under the experimental conditions used. This was determined from experiments with stand oils of various viscosities and the velocity of the sphere was found to be inversely proportional to the kinematic viscosity of the stand oil used (Fig. 9).

Further experiments indicated that the relationship between apparent viscosity and velocity of the sphere was virtually independent of the film thickness used, within the limits of practical application, provided the sphere was dropped lightly on to the surface of the film immediately after application and left with the panel in a horizontal plane during the flash-off period. The reproducibility of the results was shown to be good, three spheres being used in each experiment. Curves were plotted (Fig. 10) which gave the distance/time relationship at 100°C of a steel sphere moving in a 50 micrometer film of Epok resins D2101 and U9195 in the proportions 7:3. Epok D2102 is a hydroxylated acrylic resin supplied in xylol and *n*-butanol at a solids content of 60 per cent with a viscosity at 25°C of approximately 7.5 Stokes and an acid value of approximately 13.5 KOH/g. The velocity/time diagram was then drawn by

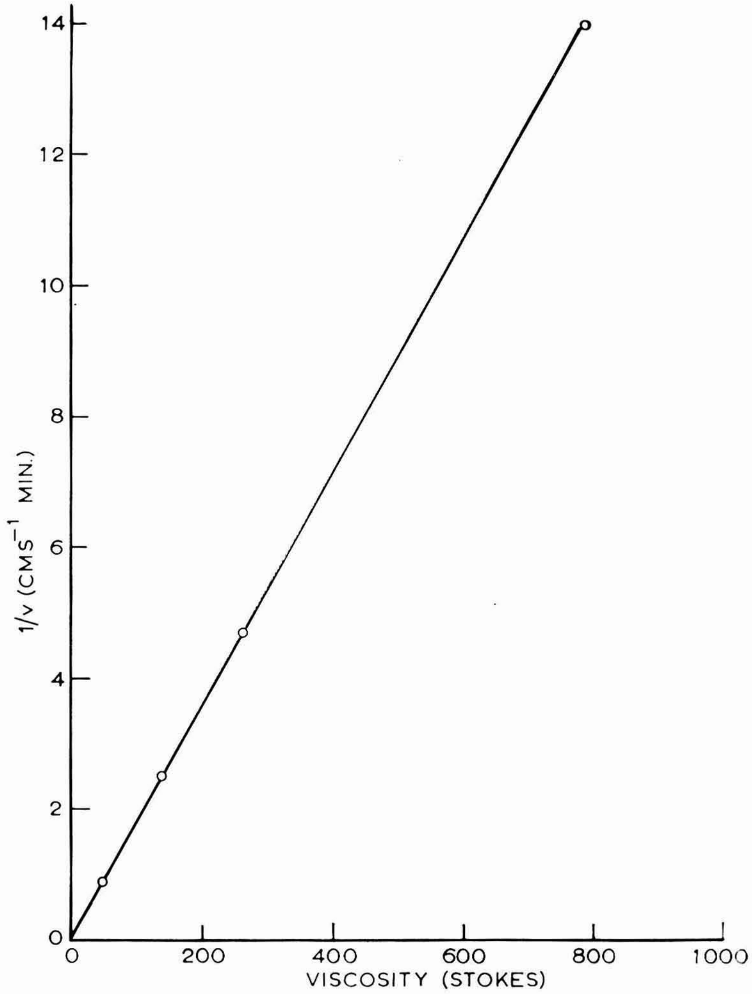


Fig. 9. Velocity of sphere vs viscosity of various stand oils

constructing tangents to the curve at various points (Fig. 11). The conversion from velocity to apparent viscosity was made from the relationship:

Apparent viscosity (Stokes) $=56/v$ (where v = velocity in centimetres per minute), obtained from Fig. 9.

The apparent viscosity/time relationships of two films based on the acrylic/melamine resins described above are shown in Fig. 12, which indicates the steeper viscosity rise of the more reactive resin, thereby rendering it unsuitable for reflow under the above conditions.

Figs. 13 and 14 indicate the apparent viscosity changes in films stoved at 130°C and 140°C respectively. At either stoving temperature, the reflow resin was higher in apparent viscosity during the initial period in the oven, as would be expected from its higher molecular weight. The increase in apparent viscosity due to crosslinking was, however, slower, which was consistent with its slower curing characteristics.

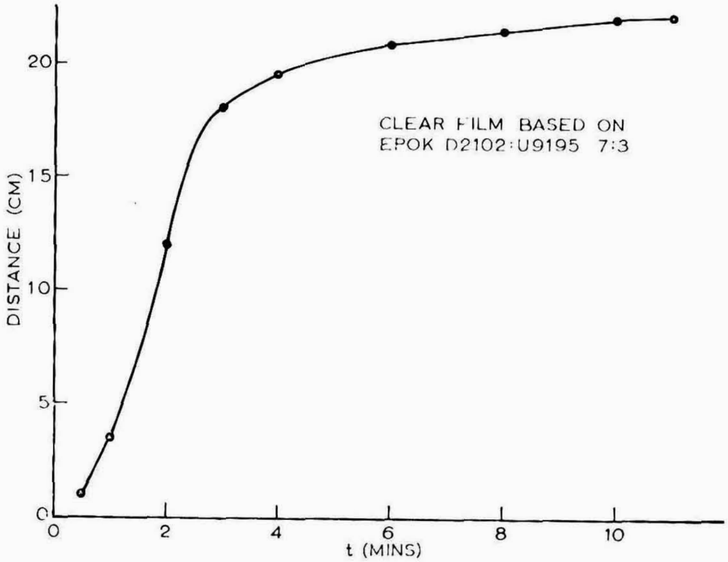


Fig. 10. Movement of sphere embedded in TSA resin film in 100°C oven

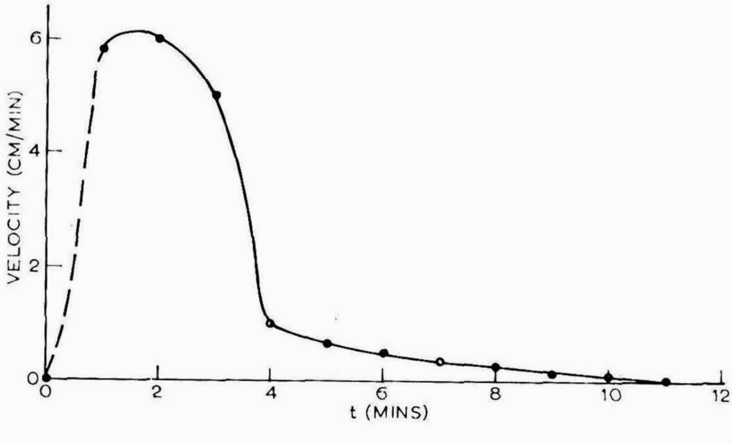


Fig. 11. Velocity of sphere embedded in TSA resin film in 100 C oven

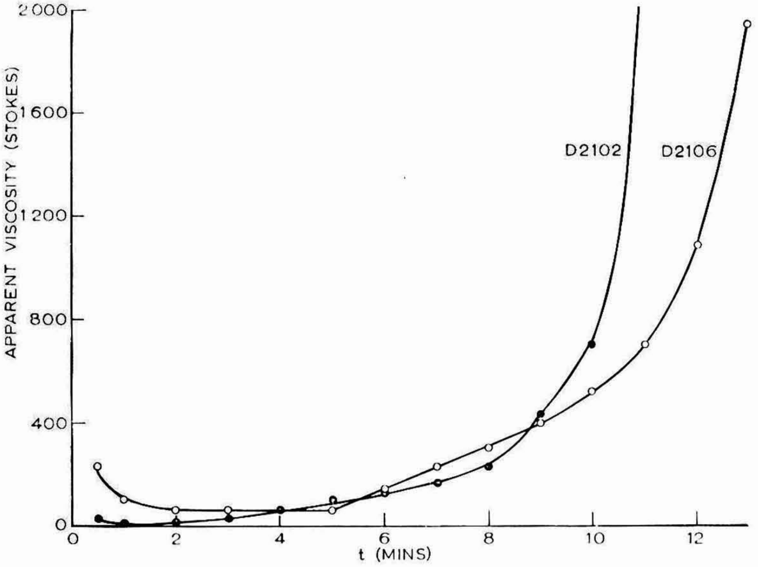


Fig. 12. Oven flow at 100°C. Reflow vs conventional TSA resin films

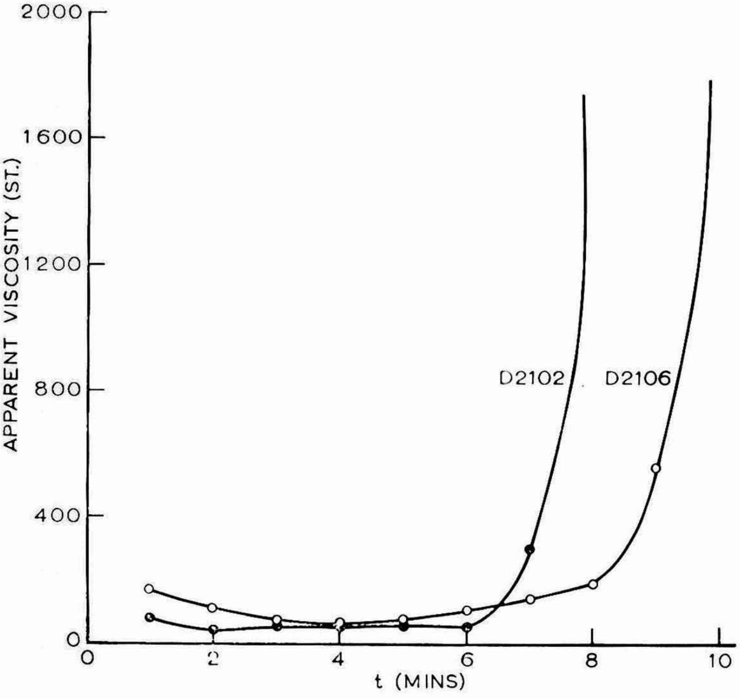


Fig. 13. Oven flow at 130°C D2102 vs D2106 films

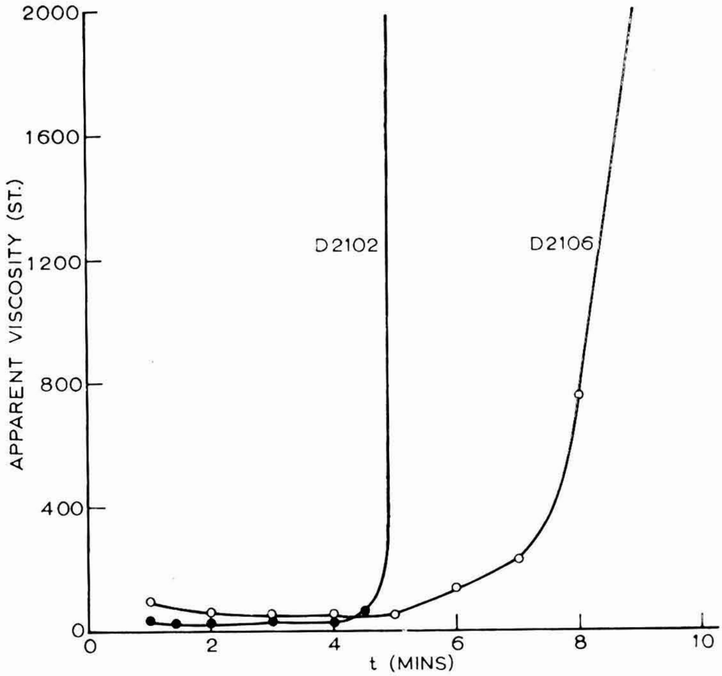


Fig. 14. Oven flow at 140°C D2102 vs D2106 films

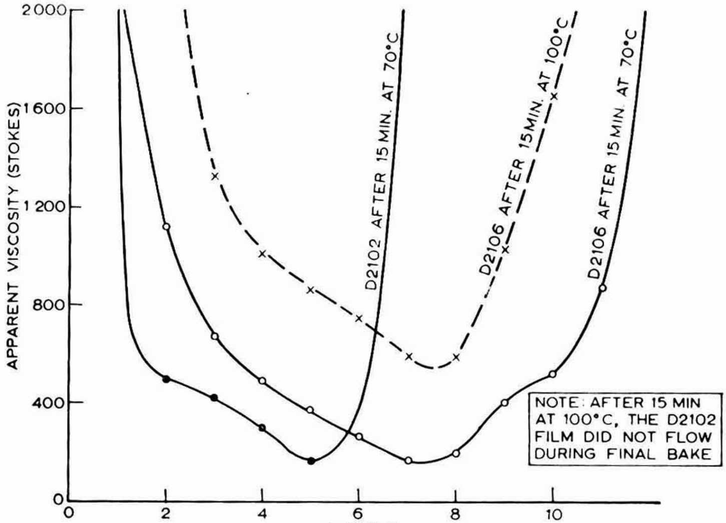
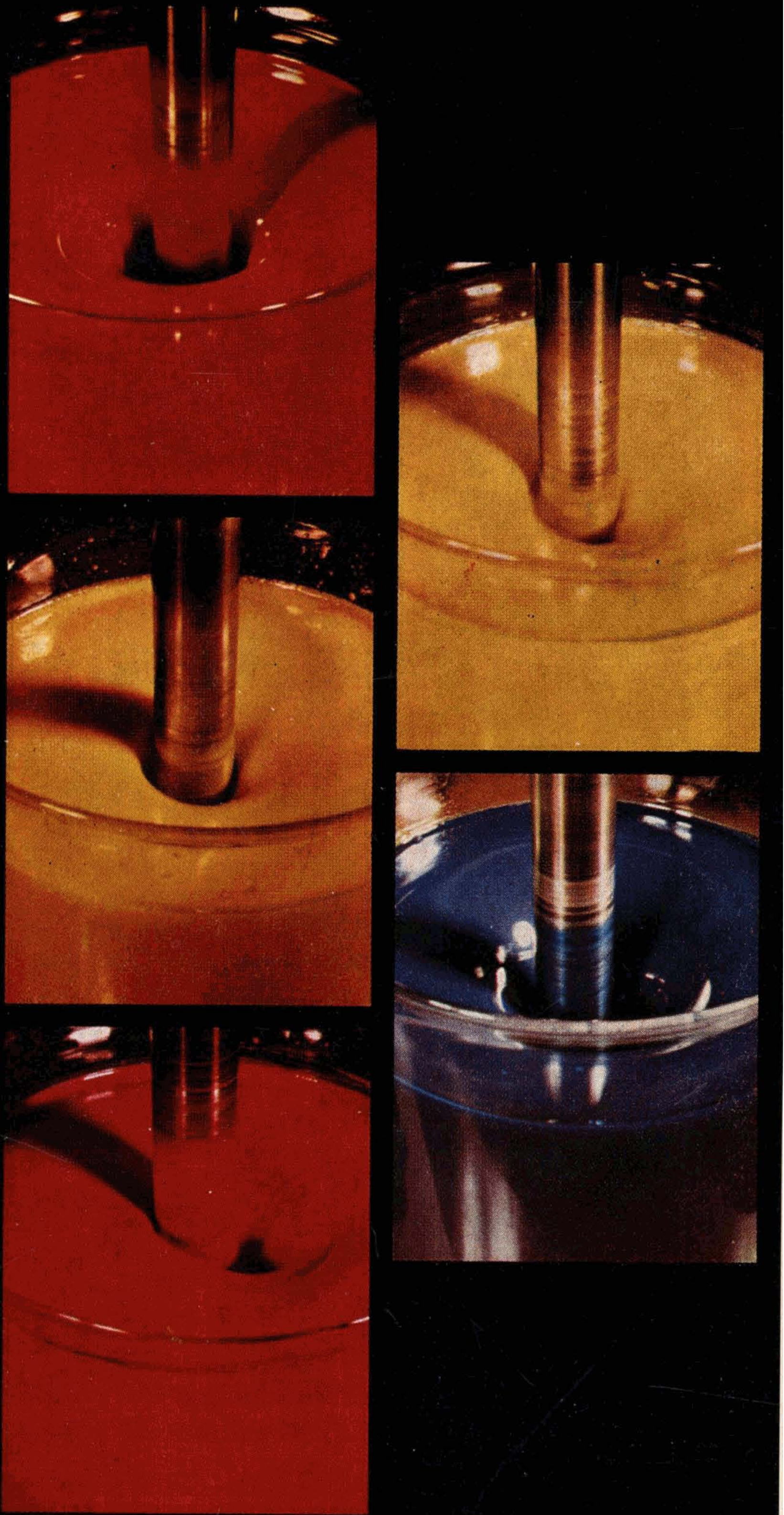


Fig. 15. Oven flow at 140°C after low temp. bakes D2102 vs D2106 films

Fig. 15 indicates the apparent viscosity changes in films stoved at 140°C after initial low temperature bakes, of 70°C in one instance, and 100°C in the other.



Films which had received an initial low bake appeared to cross-link more slowly at 140°C than those which were given only one bake at 140°C. This can be seen from a comparison of Figs. 14 and 15.

As anticipated, an initial low temperature bake of 15 minutes at 70°C prevented the reflow system from reaching as low an apparent viscosity during the final bake at 140°C as it achieved from the single stoving at 140°C.

Change in appearance owing to weathering

As an addition to the more conventional methods of assessing outside durability of paint films, Stereoscan electron microscopy now makes possible the photographic recording of film surfaces with exceptional clarity under high magnification, and this information can be used to assess weathered film surfaces.[13, 14]

Using such an instrument, the authors compared the outside durability of acrylic and alkyd/melamine enamels, in metallic pigmented films, examining unweathered, weathered, and polished surfaces, after 18 months' weathering in Florida. The alkyd/melamine system exhibited micro-checking, and it was considered possible that breakdown was associated with the geometry of the aluminium flake particles. Polishing did not completely eliminate the defect in the case of the alkyd film, and it is questionable whether the polishing process

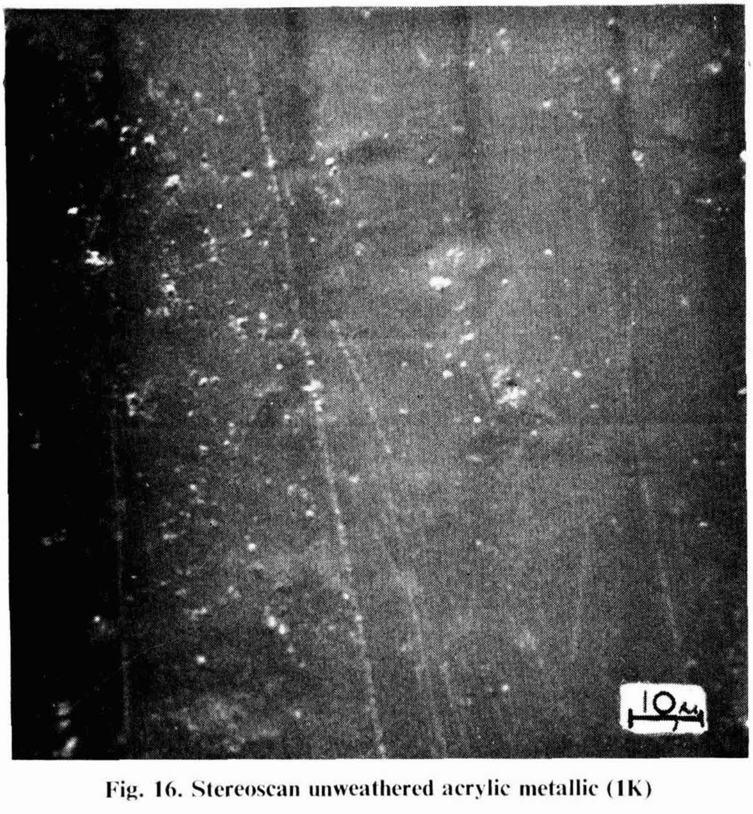


Fig. 16. Stereoscan unweathered acrylic metallic (1K)

did little more than fill in the cracks with polish. The Stereoscan photomicrographs are shown in Figs. 16-21. The corresponding weathering data is given in Fig. 22, which confirms the inferior result given by the alkyd/melamine film.

Mar resistance

Mar resistance is related, amongst other things, to the surface hardness of a paint film. In view of the large number of methods of measuring surface hardness, it is not always possible to relate these two properties. Mar resistance is usually measured empirically by the swift motion of the fingernail across the surface of the film, the resulting scratch being assessed visually.

The relationship between Erichsen pencil, Vickers diamond, and Koenig pendulum hardness of three clear acrylic/melamine films is shown in Table 1, which does not indicate a linear relationship between the hardness results obtained by these methods. No precise correlation appeared to exist between the mar resistance test by fingernail and the hardness tests mentioned above. A new method of quantitatively assessing mar resistance was therefore investigated. The test which was finally devised involved the production of a uniform scratch on the surface of the paint film under investigation, followed by the measurement of the depth of the scratch using a surface profile measuring apparatus. The uniform scratch was produced by a 3H pencil under constant

Fig. 17. Stereoscan unweathered alkyd metallic (1K)

Fig. 18. Stereoscan weathered acrylic metallic (1K)

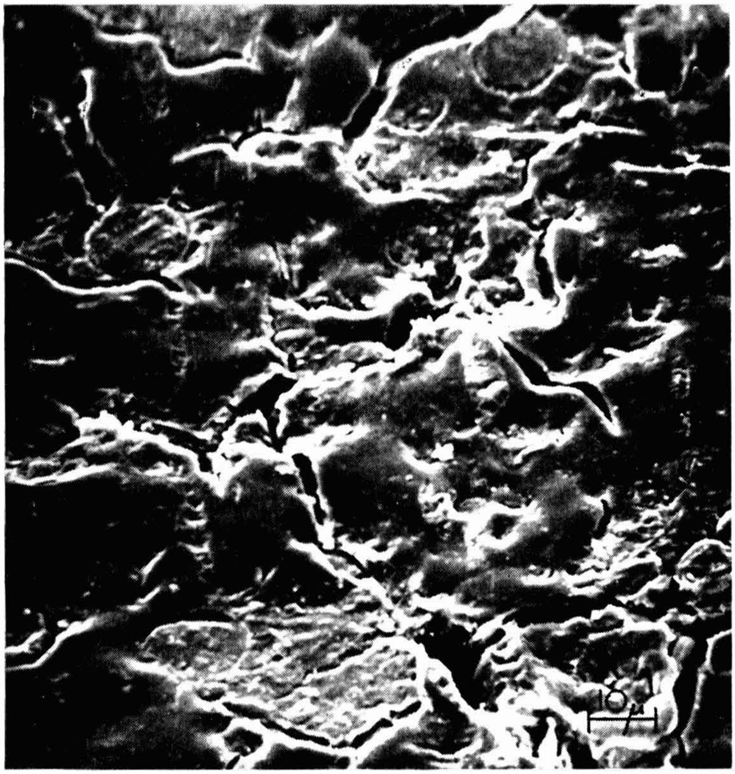


Fig. 19. Stereoscan weathered alkyd metallic (1K)

Fig. 20. Stereoscan polished acrylic metallic (1K)

Fig. 21. Stereoscan polished alkyd metallic (1K)

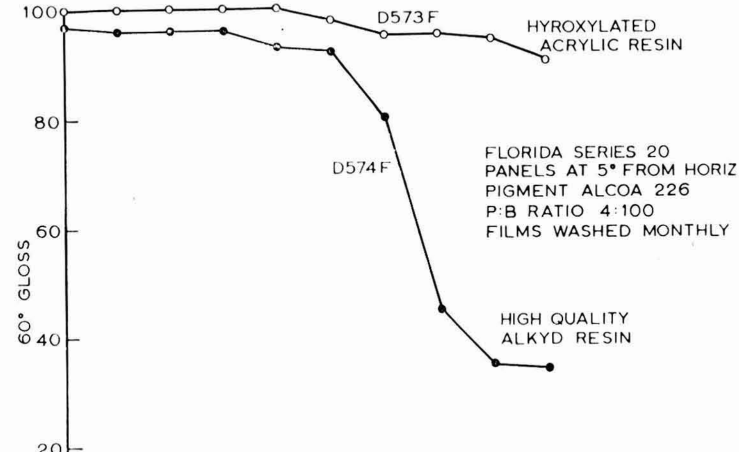


Fig. 22. Comparative weathering of metallic enamels based on acrylic and alkyd/melamine resins

load and the profile of each scratch was determined at several points at right angles to the scratch using the Talysurf instrument. The results are given in Fig. 23 which confirms the order of mar resistance obtained previously with the fingernail. Fig. 24 shows the type of trace obtained over scratches made with the fingernail, a 3H pencil, and a fine ballpoint pen. Traces made across each scratch at different points were generally found to be reproducible. The traces indicate that the fingernail and 3H pencil methods gave a rougher and more uneven indentation, which could be accounted for by the characteristics of the sliding contacts, i.e. differences in the normal and tangential forces operating at the surface. This would result in different mechanical and thermal disturbances

Table 1

Relationship between Erichsen pencil, Vickers diamond, Koenig pendulum hardness and mar resistance of clear cured TSA resin films

Film thickness	1.5 thou (dry)
Ratio acrylic:melamine resins	7:3 (based on solids)
Stoving schedule	17 minutes at 130°C

Film ref.	Koenig pendulum hardness (sec)	Vickers diamond hardness (HP25)	Erichsen pencil hardness	Mar resistance (fingernail test)
1	149	48	F	Poor
2	147	54	H	Moderate
3	183	69	2H	Good

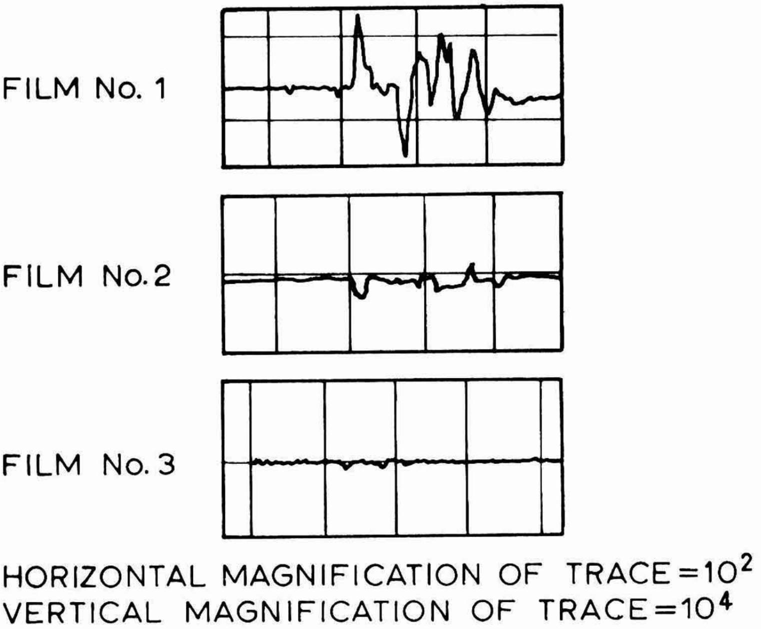


Fig. 23. Talysurf traces indicating mar resistance of three TSA resin films

at the surface of the enamel film. Kragelskii[15] has considered both molecular interaction (adhesion) and mechanical interaction (interpenetration) between two solids. In the case of a spherical indentor sliding over a plane surface, he described five ways in which the frictional bonds may be disturbed, as follows: elastic displacement; plastic displacement; cutting; trapping of the surface films and their subsequent destruction; and scuffing of the surfaces, accompanied by tearing in depth of the materials. The authors consider that fingernail or pencil marring may involve all of the above disturbances, whereas the sliding ball method may not involve the latter two or three stages.

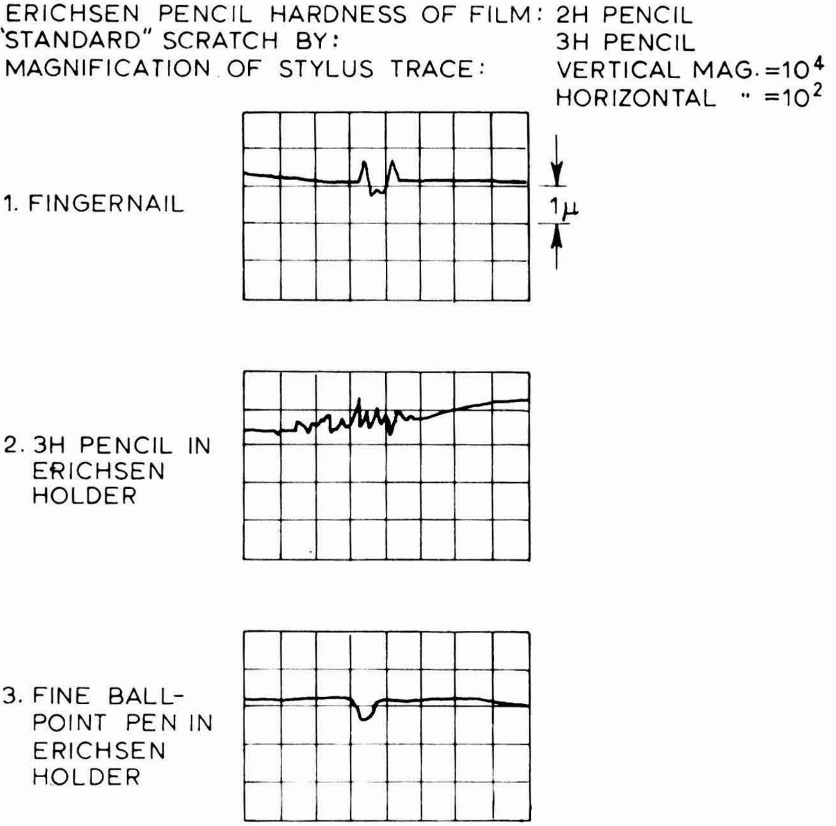


Fig. 24. Talysurf traces of (a) fingernail scratch (b) 3H pencil scratch (c) ballpoint pen scratch

The above processes are accompanied by the evolution of heat, resulting in a localised increase in temperature between the sliding surfaces. The distribution of heat will depend upon the thermal conductivities and diffusivities of each material. An estimation of the temperature rise can be derived from the theoretical and practical considerations of various workers.

Jaegar[16] has investigated in detail the heat produced between rubbing surfaces and concluded that a thin layer at the point of contact has a profound effect on the temperature rise. In his calculations he considered the mean temperature rise, which he verified experimentally. Archard[17] applied Jaegar's calculations

and derived two equations relating a dimensionless parameter, L, with the so-called flash temperature between two rubbing surfaces of bodies B and C assuming the contact area to be a stationary heat source with respect to body B and a moving heat source with respect to body C. For a stationary heat source Archard derived the expression

$$\theta_B = 0.5\ \omega_B\ L_B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

and for a moving heat source ($L > 5$)

$$\theta_C = 0.435\ \omega_C\ L_C^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In order to apply these equations to a practical example it is necessary to calculate the flash temperature for each body on the assumption that all the heat is supplied to it. The true temperature θ_M is then given by:

$$\frac{1}{\theta_M} = \frac{1}{\theta_B} + \frac{1}{\theta_C} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and where L, as defined above $= \dfrac{\nu R_1}{2\alpha}$ ....(4)

in which ν = relative speed of sliding

R_1 = radius of a single circular contact

α = thermal diffusivity

Now $\alpha = \dfrac{K}{C\rho}$ ....(5)

where K = thermal conductivity

C = specific heat

ρ = density

and $R_1 = \sqrt{A/\pi}$ ....(6)

where A = area of a single contact

From equations (4) (5) & (6)

$$L = \frac{\sqrt{\dfrac{A}{\pi}}\ C\rho}{2K} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

also $\omega = \dfrac{\pi q}{\rho C \nu}$ ....(8)

where q = rate of supply of heat per unit area

But $q = \dfrac{f N \nu}{A J}$ ....(9)

where f = coefficient of friction

N = load

J = mechanical equivalent of heat

Therefore from equations (8) and (9)

$$\omega = \frac{\pi f N}{A J \rho C} \qquad \text{.....................................(10)}$$

In the case of a thermosetting enamel film which is marred by the swift motion of a fingernail, the following numerical values might apply:

(Using suffixes F for the film and N for the fingernail)

ν = 300cm sec^{-1}

A = 5×10^{-4} cm^2 (therefore $R_1 = 1.26 \times 10^{-2}$cm)

C_F = 0.4 cal g^{-1} °C^{-1} and C_N = 0.3 cal g^{-1} °C^{-1}

ρ_F = 1 g cm^{-3} and ρ_N = 1.9 g cm^{-3}

K_F = 5×10^{-4} cal sec^{-1} cm^{-1} °C^{-1} and K_N = 5×10^{-4} cal sec^{-1} cm^{-1} °C^{-1}

f = 0.5

N = 100 g

J = 4.184×10^7 erg cal^{-1}

$$= \frac{4.184 \times 10^7}{981} \text{ g cm cal}^{-1}$$

From equations (3), (7) and (10) it is seen that

$$\frac{1}{\theta_M} = \frac{AJ}{\pi f N} \left\{ \left(\frac{K_F C_F \rho_F}{0.094 \nu R_1} \right)^{\frac{1}{2}} + \frac{2K_N}{0.5 \nu R_1} \right\} \qquad \text{...........(11)}$$

Substituting numerical values into equation 11,

$$\theta_M = 304°\text{C}.$$

The rise in temperature calculated above is significant when considering systems that show any degree of thermoplasticity. The authors have considered the decrease in hardness with increasing test temperatures of thermosetting acrylic and alkyd/melamine films. The results shown in Fig. 25 indicate that the acrylic film does, in fact, exhibit more thermoplasticity than an alkyd/melamine film, and will therefore mar more readily.

It can be seen from equation 11 that the temperature rise is directly proportional to the coefficient of friction between the two surfaces in contact, other parameters being constant. When a film is wax polished or handled with greasy

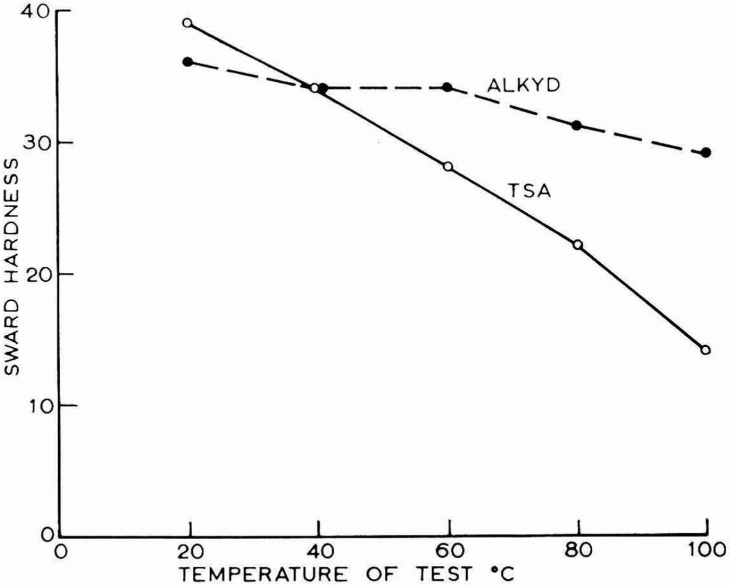


Fig. 25. Hardness vs test temperature of alkyd/melamine compared with acrylic films

fingers, the coefficient of friction is considerably reduced, which in turn will significantly increase its apparent mar resistance (Fig. 26). The authors have examined the use of an apparatus in their laboratories to study mar resistance. A fine steel ball was mounted in a holder and inserted into the automatic

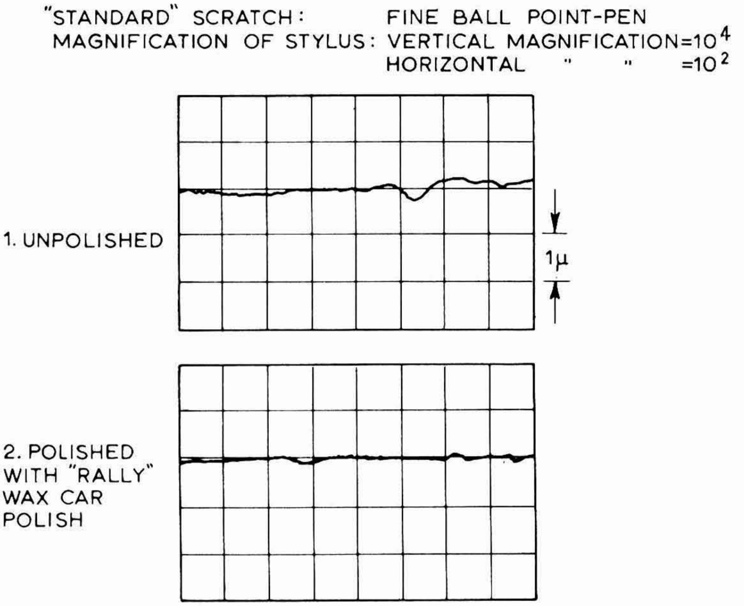


Fig. 26. Talysurf traces indicating mar resistance of polished and unpolished areas of an acrylic autobody enamel film

scratch test apparatus. This produced a uniform indentation, using a load of 500g, which could easily be studied quantitatively with a Talysurf instrument. However, it is now clear from the above considerations that this apparatus has two basic limitations:

the sliding velocity cannot be varied and is too low (3.3cm sec^{-1}) and

the thermal parameters of the steel indentor differ considerably from indentors used in practical mar resistance tests.

The methods considered to overcome these defects are: the use of a non-heat conducting indentor, and raising the temperature of the test.

Acknowledgments

The authors wish to thank the Directors of BP Chemicals International Ltd. for permission to publish this paper, their colleague Mr P. J. Fry for his help in compiling the data, and Mr K. Green, Mrs G. Brown and Mrs K. Pugh for their assistance with the experimental work.

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Discussion at the Torquay Conference

MR P. FINK-JENSEN, referring to the sliding ball technique for investigating the flow of a paint during baking, asked if the ball slid or rolled down the surface.

MR H. FOSTER said that it did both. Microscopic examination had shown that it occasionally rotated about different axes whilst sliding. Initially, it had been hoped to show a theoretical relationship between the sphere's velocity and the film viscosity, but this approach was not followed up.

MR T. R. BULLET congratulated the authors on their work on the sliding sphere technique; this was an interesting exercise in applied physics. He thought that the connection between the mechanics of the sphere's movement and Stokes Law was probably slight; it seemed more likely that the factor determining its velocity was the rate of drainage of the resin away from the surface of the sphere as it travelled down the surface. This would explain the lack of effect of film thickness on the speed of the sphere. It would be interesting to investigate the effect of changing the density of the sphere, so that the weight of the sphere could be reduced while maintaining the same geometrical relationships. It would also be interesting to see if the method could be applied to pigmented systems which were non-Newtonian in character.

Mr Foster agreed that it would be interesting to use spheres with different densities, but unless experiments were confined to constant temperature, it would be necessary to take into account the change in density of both the sphere and the film during a thermal curing cycle. The investigation suggested by Mr Bullet would certainly help to ascertain whether the density of the sphere was a material factor which affected its velocity.

Mr J. R. Taylor added that the paper had been concerned with resin viscosity which was, of course, much less complex than paint viscosity. The effect of pigment/resin interaction was something which could cause problems.

Dr J. C. Weaver referred to experimental work by Dr H. R. Moore in the USA, reported in ASTM Bulletin No. 124, 1943, 19-29 (*Chem. Ab.* **38**, 268) and US Patent 2,338,129 (1944). Using a series of plane glass plates more than 1 metre long and a steel ball about 25mm in diameter, together with levelling devices, he had evolved a method of measuring accurately the speed of a rolling ball across a test surface. Attempts had been made to establish it as an ASTM Standard Method, but it proved too laborious for buyer-seller acceptance testing. Perhaps Dr Moore's techniques could be used to make the authors' method even more quantitative, for research purposes.

Mr Foster agreed that the work would be of interest.

Mr A. G. North said that, if there were a mixture of sliding and rolling movement, errors might be caused by the formation of a thin film on the surface of the sphere which would cure more quickly than the bulk of the coating. This would accelerate the viscosity rise obtained.

Moving on to the part of the paper concerned with mar resistance testing, he was rather surprised to see that the heat caused by friction of the fingernail produced a temperature of 304°C, and also the speed of the fingernail was quoted at 300cm per second, which seemed exceedingly fast. Would the authors comment?

Mr Foster replied that the fingernail had been applied at as fast a speed as was practicable, in order to obtain the highest possible rise. It was agreed that 304°C would appear to be high, but it must be remembered that this was only a flash temperature confined to a very thin layer on the surface of the film.

Mr Taylor said that the possibility of resin curing on the surface of the sphere and then being brought back into contact with the film had been considered. It was possible that the cured material could cause a viscosity increase but, even when working with fast-curing materials, this effect did not appear to produce viscosities of the wrong order. Values had been reproducible, and were, after all, apparent viscosities intended mainly for comparative purposes. Initially, it had been hoped that the Weisenberg Rheogoniometer could have been used to measure viscosity, but this had not been possible because of the danger of damage to the instrument caused by the resin setting hard at higher temperatures. He agreed that the sphere method needed careful interpretation; no further information was available at the moment, and the method had been described in the hope that some further elucidation might be supplied by other workers.

Mr North asked if the use of a sliding plate had been considered, for instance using a microscope slide in place of the sphere. This would dispose of any possibility of cured material being reintroduced into the film.

Mr Taylor replied that this had not been attempted; the danger in such a method was that the resin cured by a condensation reaction, and condensation products could be trapped between the plates.

MR A. KJELLIN said that a CLA height of 0.05μm had been quoted in the paper as the maximum permitted surface irregularity. Did this correlate with accepted figures in practice in the automobile industry?

MR FOSTER replied that it had been chosen as the standard required by the authors, without reference to the automobile industry. The investigation was mainly to study the effects of varying the three components of the system, and the maximum irregularity chosen would not materially affect the conclusions drawn.

DR J. DUNDERDALE asked if the authors could give a gloss figure corresponding to a CLA height of 0.05μm.

MR TAYLOR said that, while it was possible to obtain such a figure in specific cases, there appeared to be no absolute relationship between CLA height and gloss. In the authors' work, a gloss finish with a CLA height of 0.05μm usually had a 60° gloss in excess of 100.

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The relationship between gloss and dispersion in acrylic paint films*

By J. H. Colling, W. E. Craker, M. C. Smith and J. Dunderdale

Laporte Industries Limited, Organic and Pigments Division, PO Box 26, Grimsby, Lincs

Summary

Preliminary work on the effect of size and dispersion of particles on the gloss of paint films is presented, using a simple acrylic system pigmented with titanium dioxide.

Silica flatting agents were added and the surfaces investigated by interference microscopy. Micro roughnesses are concluded to be responsible for the flatting action. Pre-milling of the silica affected the number of large particles present, but not the resultant gloss.

Paints without silica were milled for various times using two pigments with different crystal diameters. Electron micrographs of thin sections are used to assess dispersion. The gloss is strongly affected by relatively small dispersion changes.

The relationships involved, and the efficiencies of various sizes, are discussed in terms of a simple expression, based upon the concept that a defect produces an area of zero reflectance. This results in an exponential relationship between gloss and particle volume concentration. The presence of an optimum "size" for gloss reduction is deduced, but not directly demonstrated or quantified.

Keywords

Properties, characteristics and conditions primarily associated with:

Materials in general	*Dried or cured films*	
particle size	dispersion gloss	
Prime pigments and dyes	*Extender pigments*	*Binders, resins, etc.*
titanium dioxide	silica	acrylic resin

Le rapport entre le brillant des feuils de peintures acryliques et le niveau de dispersion pigmentaire

Résumé

On présente une étude préliminaire sur l'effet qu'exercent la grandeur et le niveau de dispersion pigmentaire sur le brillant des feuils de peinture, à savoir un simple système acrylique pigmenté avec du dioxyde de titane.

(a) On a incorporé des agents de mattage siliceux, et l'on a examiné les surfaces au moyens de la microscopie interférentielle. On conclut que le mattage est provoqué par des micro-rugosités. Broyage de la silice avant de son incorporation à la peinture influe le nombre de grosses particules mises en évidence, mais pas le brillant.

(b) Les peintures exempte de silice ont été broyées pendant de différentes périodes en utilisant deux pigments ayant les diamètres du cristal différents. Afin d'apprécier le niveau de dispersion, on a utilisé les électronmicrographies des plaques minces. Le brillant est fortement influé par des changements relativement faibles dans le niveau de dispersion.

Les rapports impliqués, et également les rendements des diverses grandeurs sont discutés sous termes d'une expression simple, où l'on conçoit que chaque défectuosité provoque une région où le facteur de réflexion est zéro. Cela fait naître un rapport exponentiel entre le brillant et la concentration pigmentaire en volume. L'existence d'une grandeur optimale au point de vue de la diminution du brillant est déduite, mais elle n'est pas demontrée directement, et on n'accorde pas une valeur spécifique à cette grandeur.

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*Presented at the Torquay Conference on 7 May 1971

Die Beziehungen Zwischen Glanz und Dispersion bei Akrylharzlackfilmen

Zusammenfassung

Vorarbeiten über die Auswirkung von Teilchengrösse und-Dispersion auf den Glanz von Lackfilmen, die aus einem einfachen mit Titanweiss pigmentierten Akrylharzzystem bestehen, werden vorgelegt.

(a) Es wurden Mattierungsmittel aus Kieselerde zugesetzt, und die Oberfläche mittels Interferenzmikrokopie untersucht. Der Mattierungseffekt wurde als Folge der verursachten Mikrorauheit angesehen. Vormahlen der Kieselerde wirkte sich auf die Anzahl der anwesenden grossen Partikel, nicht aber auf den sich ergebenden Glanzgrad aus.

(b) Lackfarben enthaltend zweierlei Pigmente verschiedenen Kristalldurchmessers, aber keine Kieselerde, wurde verschieden lang gemahlen. Elektronenmikrographien dünner Schnitte dienten zur Bewertung des Dispersionsgrades. Der Glanz wird bereits durch verhältnismässig geringe Änderungen hinsichtlich Dispersion stark beeinflusst.

Auf einfache Weise werden unter Benutzung der Vorstellung, dass eine Fehlstelle ein nichtreflektierendes Gebiet erzeugt, die gegenseitigen Beziehungen und die Auswirkungen grössenmässiger Unterschiede besprochen. Daraus ergibt sich eine exponentielle Beziehung zwischen Glanz und Partikel-Volumenkonzentration. Das Vorhandensein einer Optimum-"grösse" für Glanzminderung wird gefolgert, aber nicht direkt demonstriert oder quantifiziert

Зависимость между лоском и дисперсией в акриловых красочных пленках

Резюме

Описывается предварительное исследование влияния величины и дисперсии частиц на лоск красочных пленок, применяя простую акриловую систему пигментированную двуокисью титана.

(а) Добавлялись матировочные средства двуокиси кремния и поверхности исследовались при помощи интерференционной микроскопии. Считается что микро-шероховатости ответственны за матировочное действие. Предварительное измельчение двуокиси кремния влияло на число наличных крупных частиц но не оказало влияния на результирующий лоск.

(в) Краски без двуокиси кремния раздроблялись в течение различных периодов времени, применяя два пигмента с различными диаметрами кристалла. Используются электронные микроснимки тонких срезов для оценки дисперсии. Относительно малые изменения в дисперсии сильно влияют на лоск.

Обсуждаются полученные отношения и эффективность различных размеров частиц, применяя простое выражение основанное на понятии что дефект вызывает площадь нулевой отражаемости. Это приводит к экспоненциальной зависимости между лоском и объемной концентрацией частиц. Формулируется наличие оптимального «размера» частиц для снижения лоска, хотя оно не демонстрируется и количественно не определяется.

Introduction

The factors that influence the assessment of gloss have been discussed in a number of papers[1, 2, 3, 4]. In an earlier work[5], the authors have examined the relationship between subjective gloss assessment and objective measurements made with a 45° fixed head gloss meter (EEL) and with measurements made on a specially constructed spectrogoniophotometer (SGP).

The optics of the SGP are such that a perfectly plane surface gives rise to a recorder trace which is triangular and which has a fixed base width. Deviations from perfection will alter the shape or size of the triangle. Sample plates are compared with a standard black glass tile, the results being expressed in terms of peak height ratio (PHR) and peak area ratio (PAR), the latter being the less precise measurement. Each of these ratios can be affected by surface distortions which were[4], for the sake of convenience, designated micro or macro according to the manner in which they affected the incident light beam.

Micro defects are of a size such that the incident radiation is scattered or diffracted and does not, therefore, contribute to the specular beam. The SGP peak remains triangular, but both the PHR and PAR are reduced. By analogy with conventional scattering theory, these defects are expected to be of the same order of size as the wavelength of the incident radiation. These micro defects result in low image contrast when the surface is used as a mirror, but the image remains sharp.

Macro defects, on the other hand, reflect energy away from the main specular beam in accordance with the laws of geometric optics. Thus, the total energy in the specular beam remains unaltered, but it is spread over a wider angle. The PAR remains unaltered, but the PHR decreases and the image is distorted.

Obviously, these two sizes of defect are merely extremes of what is essentially a continuous range and surfaces can contain any combination of defects so that a wide range of peak shapes is possible.

A triangular peak with "tails" is commonly observed, resulting from the presence of a few macro distortions in a surface which otherwise contains only micro distortions, or is perfectly plane. Gross macro distortions result from the presence of very large defects and/or the method of application or drying. In the present work, care was taken to prevent confusion of the results by these defects.

Although it is generally accepted[6, 7, 8, 9] that size and dispersion differences of particles in paints lead to different levels of gloss, the actual size of particles, and the nature of the relationships involved, have not been defined. This work, based on the methods outlined previously, is the first part of a detailed study of the relationships between the gloss of paint systems, the surface defects responsible for reduced gloss, and the degree of dispersion of pigment particles within the films. A simple acrylic system (Bedacryl 122X) pigmented with titanium dioxide was used throughout.

The present work consists of two main parts:

a study was made of the effect of adding silica flatting agents;

a study of the effect of variation in the degree of dispersion of titanium dioxide in terms of scattering coefficient and gloss was made by milling the paints for different times, the pigment particle groupings within the films being measured from electron micrographs of thin sections.

Experimental

Silica additions

A set of paints containing various quantities of fine silica was prepared. Five grades of silica, designated (A) to (E), were incorporated into standard acrylic paints.

Paint mill base (15% PVC):

10g titanium dioxide	Milled for 16 hours in 4oz jars at 180 rpm, diluted with 30g medium and rolled for 1 hour
30g medium	
100g $\frac{3}{8}$in steatite ballotini	

Silica mill base:

10g fine silica	Milled for 1 hour in a 16oz jar at 120 rpm, diluted with 200g medium and rolled for a further $\frac{1}{2}$ hour
90g medium	
200g $\frac{3}{8}$in steatite ballotini	

The medium in each case consisted of 2 parts Bedacryl 122X : 1 part xylene by weight.

The silica additions were made by replacement of the titanium dioxide in the range 0-10 per cent by weight (0-3.85 per cent total paint weight), with the appropriate quantity of each silica.

Paint films were prepared in duplicate by spinning on to 6in × 4in glass plates. One panel of each paint was dried normally (paint film uppermost) and the other was dried in an inverted position. Each panel was examined by SGP at 550nm; EEL gloss measurements were made and interference micrographs of the surfaces were obtained.

Pre-milled silica additions

An additional series of silica-containing paints was prepared using samples of silica mill base which had been milled for different times, the manner of preparation and measurements made being as described previously.

Paints containing TiO_2 only

Paints were prepared from two untreated rutile titanium dioxide pigments, the volume-biased mean crystal diameters of which were 0.22μm and 0.17μm for pigments (A) and (B) respectively. A number of jars were prepared and milled for different times, the pigments being added in an incremental fashion. For practical reasons, the actual times deviated slightly from those shown below (see Table 3).

10% PVC mill base:

10.4g titanium dioxide	Milled for 6, 16, 32, 64, 150 and 500 hours in 8oz glass jars at 144 rpm, diluted with 47.3g medium and rolled for 1 hour
47.3g medium (as before)	
150g $\frac{3}{8}$in steatite ballotini	

20% PVC mill base:

23.5g titanium dioxide	Milling conditions as above
47.3g medium	
150g $\frac{3}{8}$in steatite ballotini	

Paint films were prepared on glass plates as before. In addition, separate films were prepared on Melinex using a no. 8 wire wound applicator. Small strips of these films were cut and embedded in an Araldite resin, and sections of 0.1μm nominal thickness were obtained for electron microscope transmission photographs. These paint films were also used for making scattering coefficient determinations.

Results

Effect of different silicas

The SGP peaks for all samples in this series were essentially triangular and the peak width at half peak height was constant, hence there was excellent agreement between SGP and EEL gloss measurements. Because of this agreement, EEL gloss is in general quoted in tables and graphs, since it is the more familiar measurement. In a few cases, small thin tails were observed, which are considered to be due to the presence of a small number of relatively large macro defects. There were no differences in the results obtained between the inverted and normal drying experiments, Fig. 1. Plots of EEL gloss versus weight per cent of silica are presented in Fig. 2.

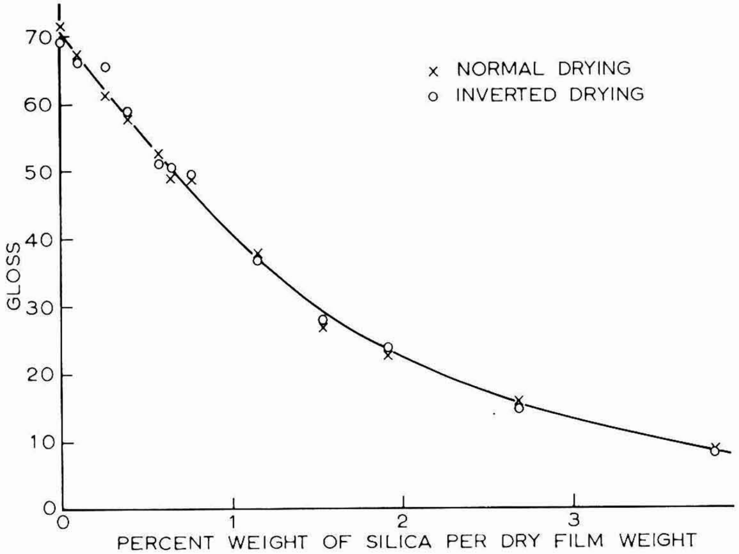


Fig. 1. EEL gloss for acrylic paints containing various amounts of silica A

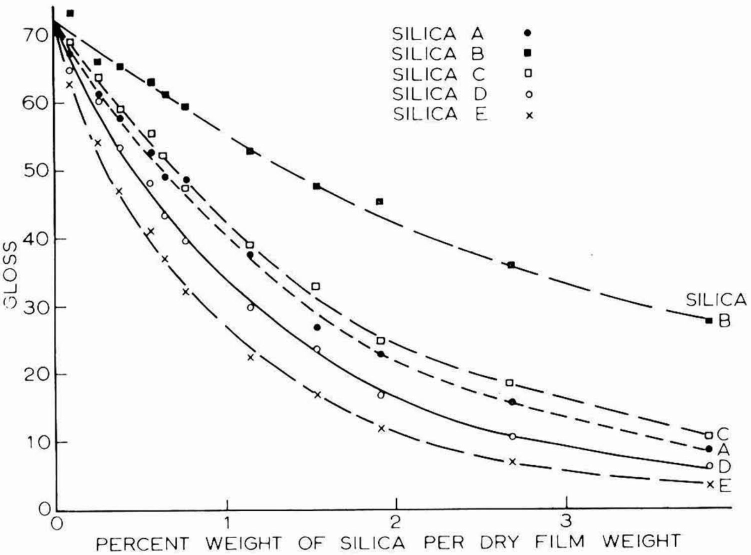


Fig. 2. EEL gloss for acrylic paints containing various amounts of the silicas

Typical areas of photographs obtained with the interference microscope are shown in Fig. 3 (the silica addition in each case was 0.57 per cent by weight). The high frequency irregularity of the interference fringes, which are essen-

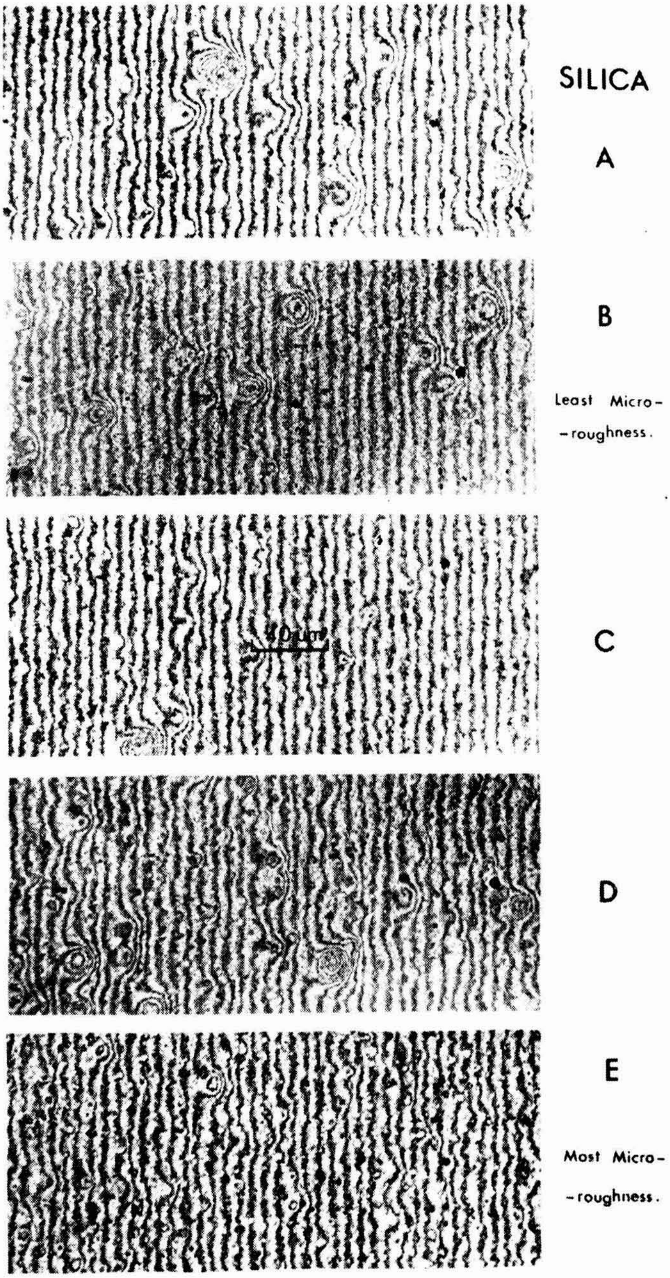


Fig. 3. Part of typical interference micrographs for 0.57% by weight (0.34% by volume) additions of the five grades of silica

tially straight, can be used to assess the surface micro roughness. A quantitative estimation may be made by measuring the coefficient of variation[4]. Macro defects can also be seen in the photographs as circular contour fringes and the number of fringes in each case can be used to estimate the size of the irregularity.

The various gloss measurements and the coefficient of variation of line spacing are given in Table 1. Fig. 4 is a plot of the coefficient of line variation against EEL gloss, from which it can be seen that the correlation is very good (significant at the 95 per cent level), confirming the hypothesis that loss of radiation from the specular beam is brought about by micro roughness of the

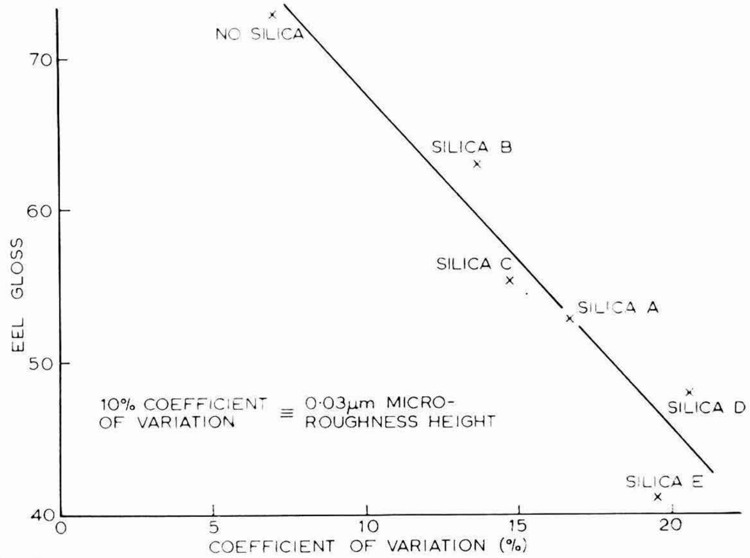


Fig. 4. EEL gloss vs micro-roughness for additions of the five silicas of 0.57% of total paint weight

Table 1

Measurements on the interference micrographs related to gloss data for paints containing 0.57% *silica*

Silica	PHR (550nm)	EEL gloss	Gloss rank	Coefficient of variation (%)	Rank	Visual ranking of macro roughness	SGP mean peak base width at 400nm (cm)	Rank
A	33.5	53	3	16.7	3	5 (most)	8.7	5
B	47.3	63	1	13.7	1	2	6.4	3
C	37.0	55	2	14.7	2	3	8.2	4
D	28.0	48	4	20.6	5	4	5.5	2
E	26.0	41	5	19.6	4	1 (least)	2.6	1

surface. A visual assessment of the macro roughness of each surface was made from the photographs and this, together with the mean peak base width, is also included in Table 1. It can be seen that there is no relationship between macro roughness and gloss, but that the agreement between macro roughness and mean peak base width is good.

Effect of adding silicas pre-milled for different times

Interference photographs of paints prepared in this series show that the macro defects decrease in size and number as a function of milling time, but there is little change in the micro defects.

Measurements obtained from the SGP peaks are given in Tables 2a and 2b. It can be seen that the peak base widths decrease with milling time, whereas the EEL gloss data given in Table 2b show little change. This, taken in conjunction with the constancy of the coefficient of variation, is again consistent with the proposition that micro roughnesses are responsible for low gloss.

Table 2a

Peak base widths for paints containing 0.77% silica

Milling time (hours)	Mean base width (cm)
0	8.6
½	7.7
1	6.7
2	5.9
6	5.1
16	3.9

Table 2b

Mean EEL gloss results for paints containing silica A pre-milled for various times

Milling time (hrs)	Weight % silica per weight of dry paint				
	0.093	0.385	0.769	1.92	3.85
0	67	59	48	23	8
½	68	60	47	23	10
1	67	59	50	23	8
2	67	60	45	21	8
6	66	58	45	22	8
16	68	56	41	21	8

Paints containing titanium dioxide only

In this series of experiments, the gloss was altered by varying the PVC and the type of pigment. The manner in which the paints were prepared also produced changes in dispersion. The EEL gloss measurements are given in Table 3 for each of the pigments used, at each PVC.

Table 3

EEL gloss values and peak height ratios at 550nm for various milling times

Milling time (hours)		Pigment A				Pigment B			
		10% PVC		20% PVC		10% PVC		20% PVC	
Nominal	Actual	EEL	PHR	EEL	PHR	EEL	PHR	EEL	PHR
6	6.2	49	34	22	9	47	30	19	6
16	16.7	56	43	30	20	59	42	34	21
16 Dup.		53	41	28	17	53	42	27	15
32	29.5	62	53	35	25	60	50	34	22
64	66.9	70	58	40	31	67	58	43	34
64 Dup.		68	61	42	33	67	60	43	34
150	148.5	75	71	52	44	73	68	53	45
500	504.5	82	79	71	67	81	77	66	60

The EEL glosses are plotted against the log of milling time in Fig. 5 and it can be seen that, for the range of milling times used, there is an approximately linear relationship. It is evident in this presentation that the gloss is strongly dependent on PVC (as would be expected), but does not differ much between the pigments. The pattern shown by the plot of PHR against milling time, Fig. 6, is seen to be very similar to that shown in Fig. 5. Once again, the EEL gloss and PHR are in excellent agreement.

Thin section photographs of areas typical of both pigments at each PVC are presented in Fig. 7. By counting the number of primary particles in any group (a group is a collection of particles in which each particle is in contact with at least one other particle), an attempt has been made to assess the group size distribution and hence the mean group size; that is, the mean number of particles in a group is used as an estimate of group size.

It is considered that these means are a valid measure of the dispersion of the pigment; this is discussed later. The various means for all paints are given in Table 4, together with milling times, EEL glosses and scattering coefficients.

It can be seen that the group size bears an inverse relationship to the EEL gloss and the results are plotted in Fig. 8.

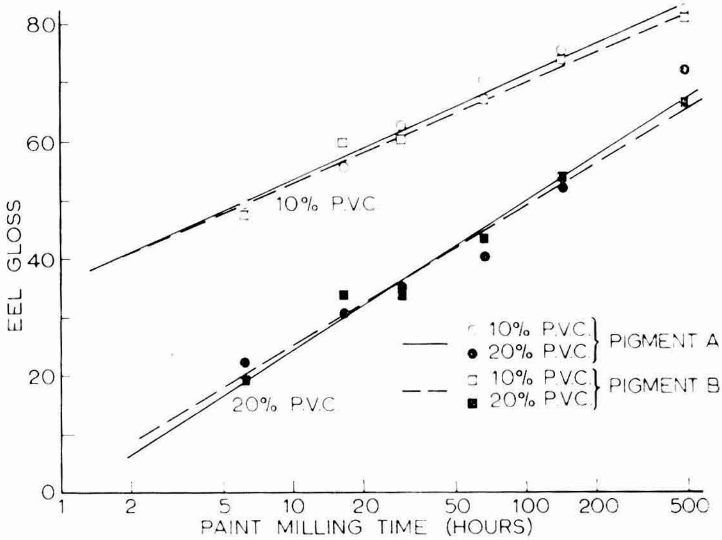


Fig. 5. EEL gloss vs milling time at 10% and 20% PVC

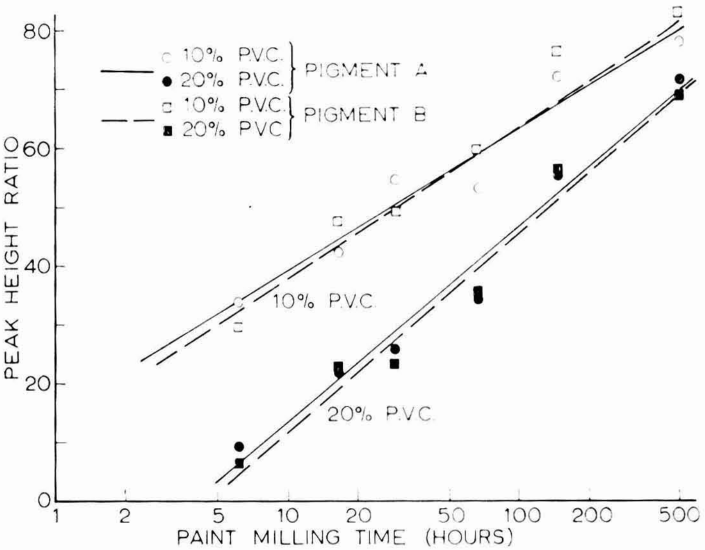
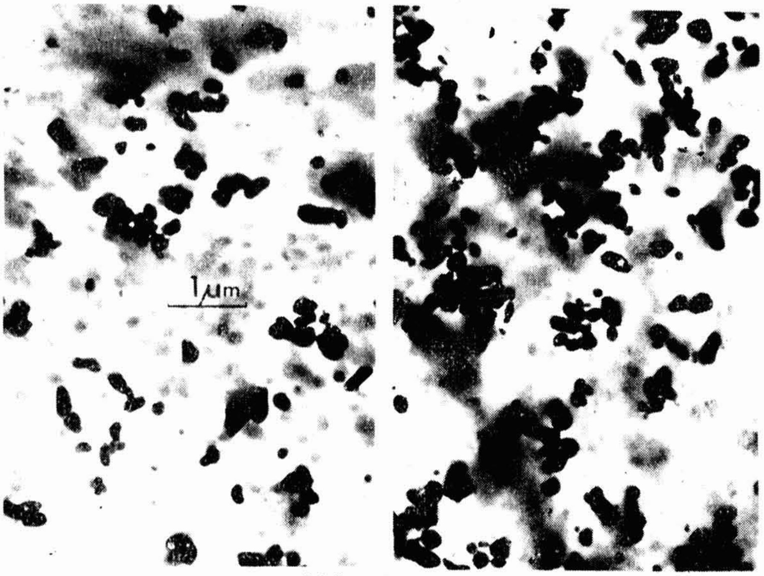


Fig. 6. Peak height ratio at 550nm vs milling time at 10% and 20% PVC

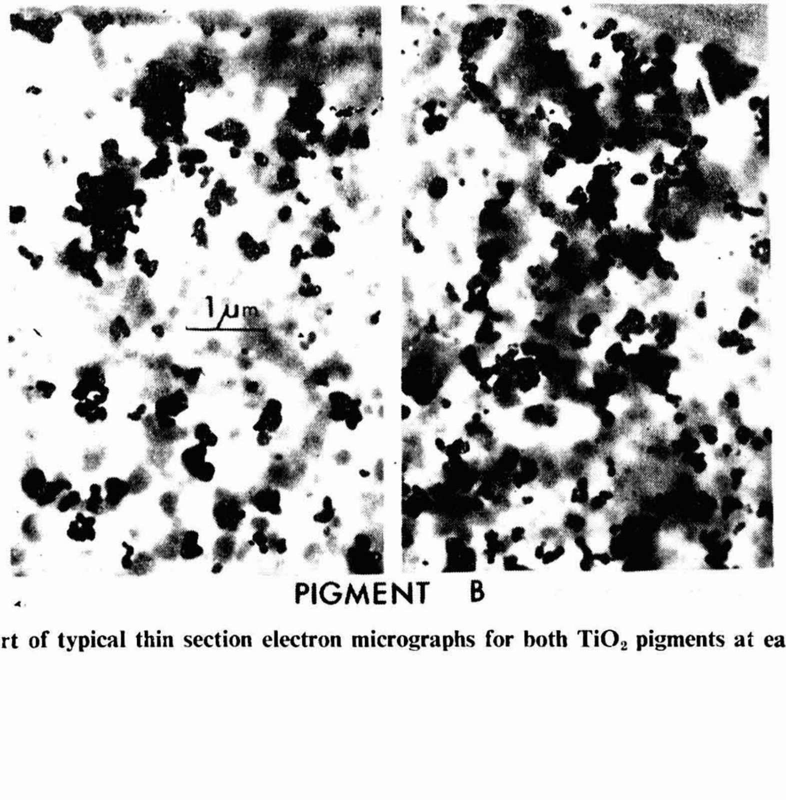
It has been found that similar relationships may be observed if the proportion of particles present as singlets is used as a measure of dispersion rather than the mean group size.

It has also been observed that a similar relationship holds between gloss and mean group size if paints prepared from pigments of different dispersibility, but milled under identical conditions, are compared. A typical plot for such a series of pigments is given in Fig. 9.



PIGMENT A

10 P.V.C. 20% P.V.C.



PIGMENT B

Fig. 7. Part of typical thin section electron micrographs for both TiO_2 pigments at each PVC

Table 4. Variation in mean group size, EEL gloss and scattering coefficient with milling time

Pigment PVC	Nominal mill time	Mean number per group	EEL gloss	Scattering coefficient (mil^{-1})
A 10%	6	3.31	49	3.42
	16	2.81	56	3.31
		2.45	53	3.33
	32	2.87	62	3.43
	64	2.44	70	3.88
		2.82	68	3.77
	150	2.35	75	4.22
	500	2.30	82	4.26
A 20%	6	3.20	22	4.45
	16	3.82	30	4.55
		3.24	28	4.56
	32	3.04	35	4.41
	64	3.23	40	4.95
		3.08	42	4.93
	150	2.82	52	4.90
	500	2.18	71	5.20
B 10%	6	4.31	47	3.44
	16	3.84	59	3.56
	32	4.04	60	3.66
	64	3.32	67	3.74
		3.39	67	3.75
	150	3.16	73	3.86
	500	2.71	81	4.10
B 20%	6	5.06	19	4.26
	16	5.30	34	4.29
	32	4.78	34	4.61
	64	4.71	43	4.42
		4.68	43	4.62
	150	3.68	53	4.51
	500	3.76	66	4.71

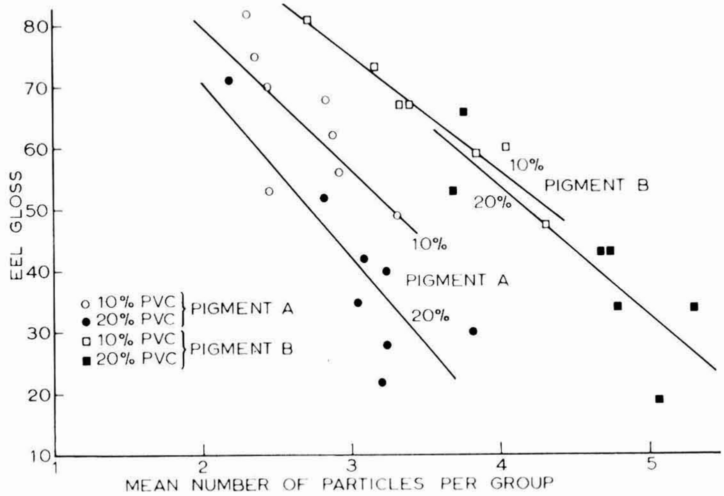


Fig. 8. EEL gloss vs mean number of particles per group (from counts on thin section micrographs)

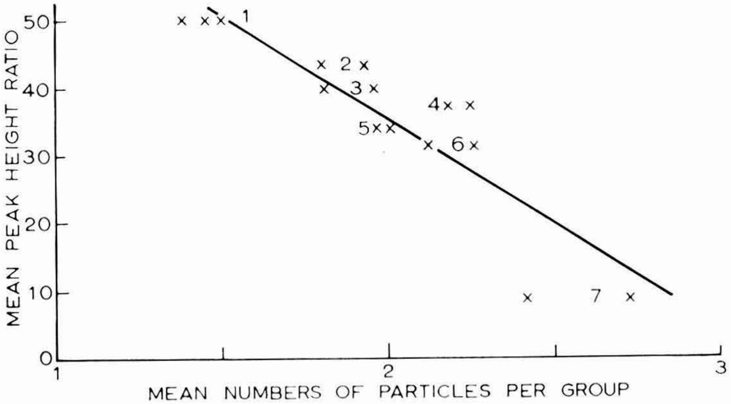


Fig. 9. Peak height ratio at 550nm vs mean number of particles per group for a range of pigments at 15% PVC

Discussion

It is generally accepted that a surface has low gloss if energy is removed from the specularly reflected beam (hence the use of instruments such as the EEL gloss meter). Although gross surface defects will produce image distortion and thereby result in a less acceptable subjective gloss, it is the small surface defects which remove energy by scattering and/or diffraction. Unfortunately, an analytical solution of Maxwell's equations appropriate to the boundary conditions that occur at a surface has not yet been proposed. However, it is not unreasonable to suppose that, by analogy with the Mie solutions, the scattering efficiency of surface defects will be strongly dependent on both the wavelength of the incident radiation and the size of the defect. It is also considered likely that there will be an optimum size of defect for scattering which will be of the same order of magnitude as the wavelength of the incident radiation. These assumptions have been used as the basis for the following simplified treatment, which is useful in discussion of the results obtained.

Consider a paint film to contain a weight W of pigment per unit volume. Let there be a weight fraction w_i of particles each having a diameter d_i and a porosity p_i, the particles being either singlets or groups of singlets. If the true density of the pigment is ρ, then the number of such particles which can interfere with unit area of surface is:

$$\frac{3W}{\pi\rho}\ \frac{w_i}{(1-p_i)d_i^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Each point of interference produces a surface defect which will scatter or diffract radiation out of the specular beam. In principle, each defect can be regarded as an area of surface which has zero reflectance as far as specular energy is concerned. Let $k(d_i\lambda)$ be the average effective area of zero reflectance for all particles of diameter d_i at wavelength λ. This function is considered to be analogous to $Q_{ext}\pi r^2$ which is used in the three-dimensional Mie theory, where Q_{ext} is the extinction coefficient and r is the radius of the particle. That is, the effective zero area can be larger than the geometric size of the surface defect.

Clearly, areas such as the one described can overlap, particularly when there is a high density of such areas. Consequently, the effectiveness of a total number, from the point of view of scattering, will be less than if all the areas were completely separated. Therefore, consideration has to be given to the probability that any particular point on the surface will be unaffected by the neighbouring defect. This is given by:

$$P_i = \exp - \frac{3W}{\pi\rho} \frac{w_i}{(1-p_i)d_i^2} k(d_i\lambda) \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In order to make the expression completely general, it is necessary to perform a summation over all the particle sizes present and expression (2) becomes:

$$P = \exp - \frac{3W}{\pi\rho} \sum_i \frac{w_i}{(1-p_i)d_i^2} k(d_i\lambda) \qquad \ldots\ldots\ldots\ldots (3)$$

If G_0 is the specular reflectance of the surface when there are no defects present, then the measured specular reflectance with defects is:

$$G = G_0 \exp - \frac{3W}{\pi\rho} \sum_i \frac{w_i}{(1-p_i)_i d^2} k(d_i\lambda) \qquad \ldots\ldots\ldots (4)$$

Dependent on the assumptions made, it is possible to derive other expressions, but all are formally identical to equation (4). They are all very difficult to use, however, because of the problems associated with the evaluation of the function $k(d_i\lambda)$.

The use of expression (4) for the purpose of discussion is made easier if the particulate system is considered to be mono-disperse—in which case it can be written:

$$G = G_0 \exp - \frac{3V}{\pi} \cdot \frac{k(d\lambda)}{d^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where V is the PVC expressed as a volume fraction.

In Fig. 10a, a possible variation of $k(d\lambda)$ (analogous to the Mie Q_{ext}) is compared with d^2, plotted against d. The resulting plot of $k(d\lambda)/d^2$ shows a pronounced maximum (Fig. 10b). It is not necessary for $k(d\lambda)$ to have an absolute maximum; an inflection produces similar results (Figs. 11, a and b). The Fig. 10 case has an expanded diameter scale, but in both a rapid rise in $k(d\lambda)$ is shown at low d, and $k(d\lambda)$ is assumed to approach the geometric area d^2 at high values of d. For both these cases, values of G/G_0 are plotted against diameter, d, for various PVCs in Fig. 12, and definite minima are observed. The results which have been obtained in this work can now be discussed in terms of this simple theoretical treatment.

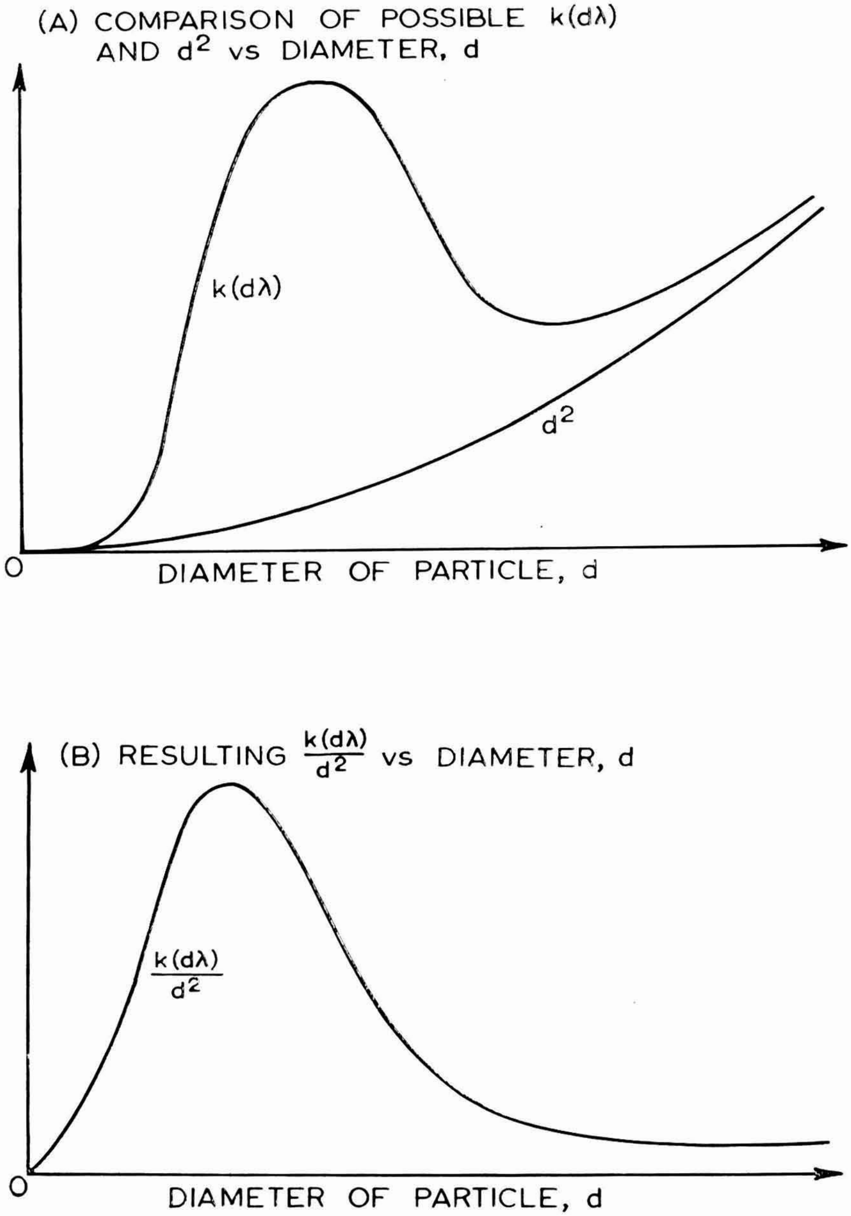
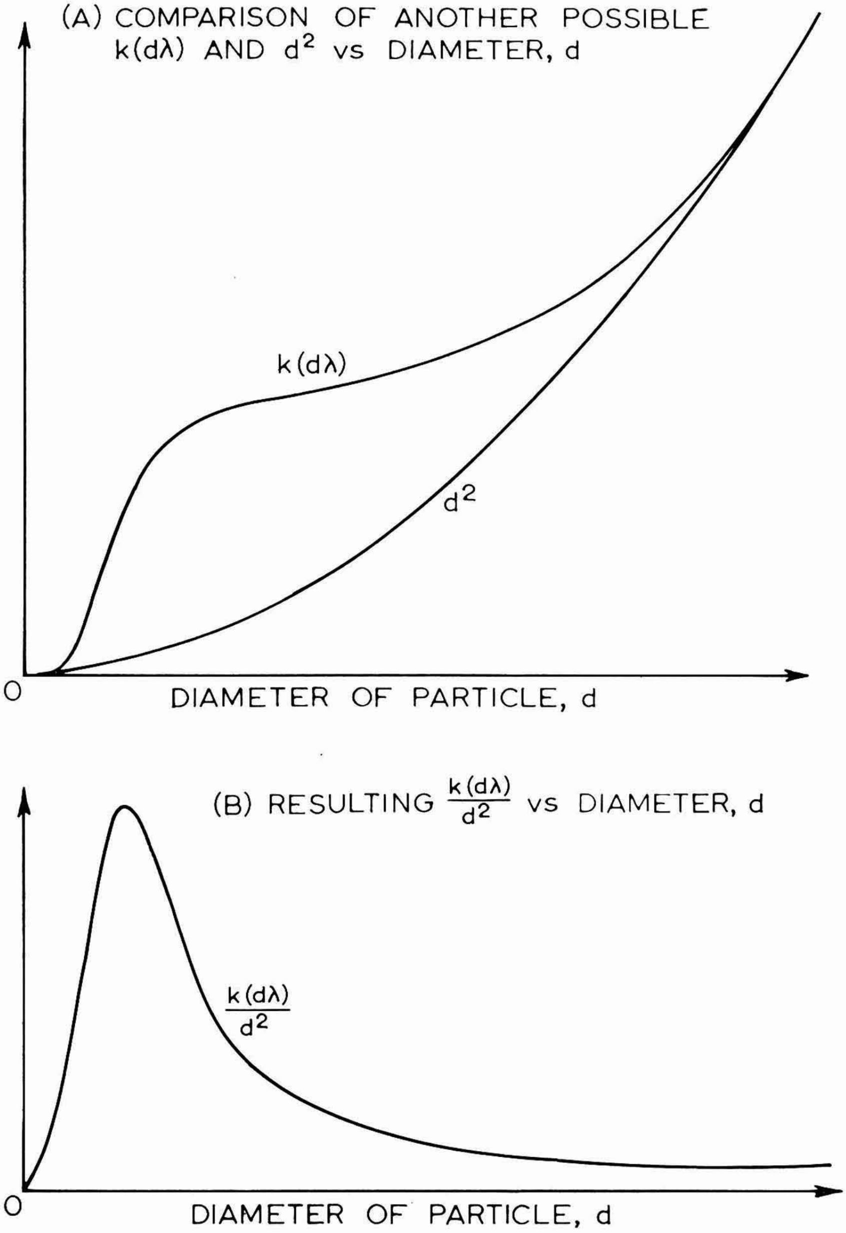


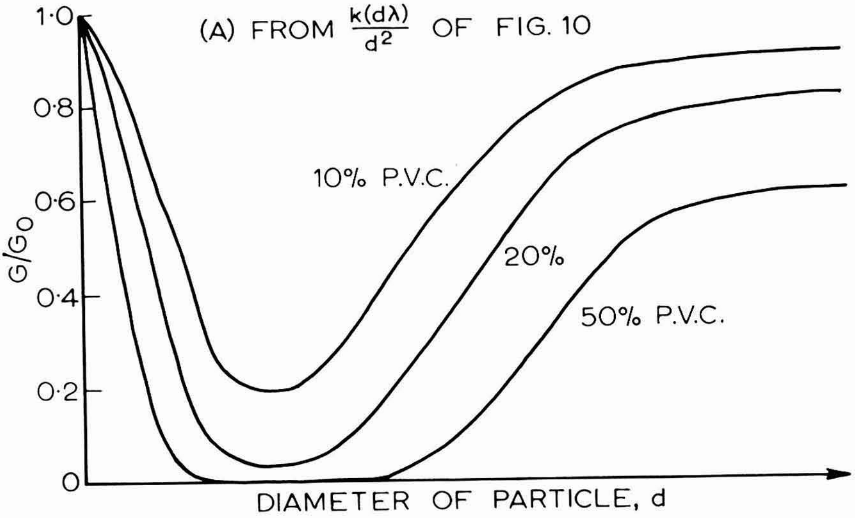
Fig. 10. Comparison of $k(d\lambda)$ and d^2 vs d, showing maximum value obtained for $\frac{k(d\lambda)}{d^2}$ vs d



(A) COMPARISON OF ANOTHER POSSIBLE $k(d\lambda)$ AND d^2 vs DIAMETER, d

(B) RESULTING $\frac{k(d\lambda)}{d^2}$ vs DIAMETER, d

Fig. 11. Example of inflexion in curve of $k(d\lambda)$ vs d producing maximum in $\frac{k(d\lambda)}{d^2}$ vs d



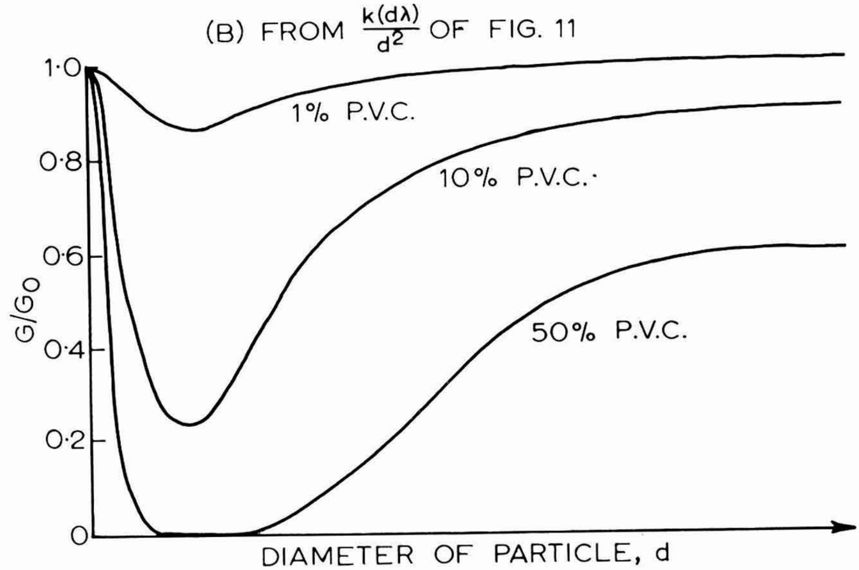


Fig. 12. Gloss ratios G/G_0 at various PVCs vs diameter, d

From Fig. 13 it is evident that an exponential relationship between the PVC of silica and the gloss exists for the paints containing silica. Each of the silicas is extremely efficient in reducing gloss and the values of $k(d\lambda)/d^2$ range from ~40 for the least efficient to ~140 for the most efficient. The plot of EEL gloss against coefficient of variation (Fig. 4) has been combined with a plot of gloss against coefficient of variation previously reported[4] and the composite plot is presented in Fig. 14. The agreement between the two sets of data indicates that the same physical process is responsible in both cases.

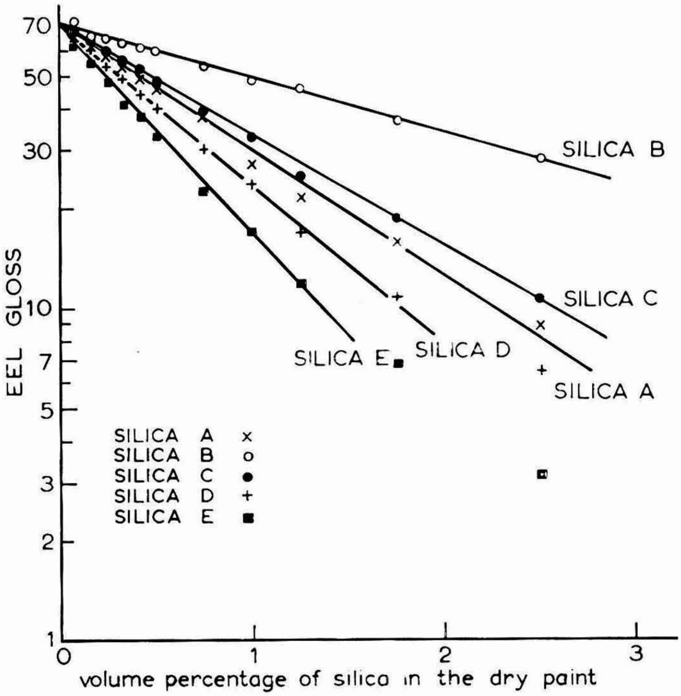


Fig. 13. EEL gloss (log scale) vs volume percentage of silica

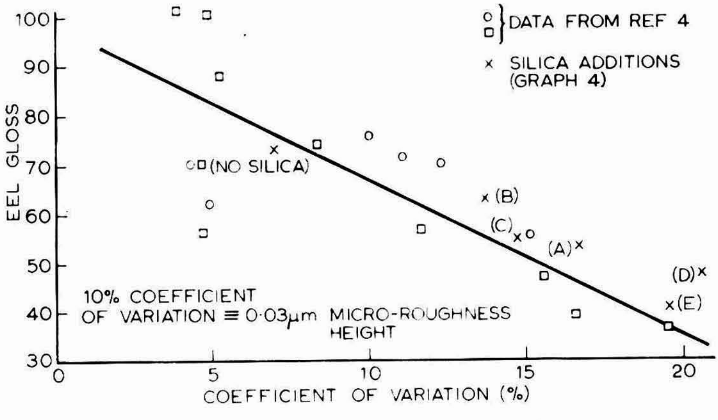


Fig. 14. EEL gloss vs coefficient of variation (from interference micrographs)

Referring to the paint made from pigments A and B, it has been shown that gloss increases with milling time (Figs. 5 and 6) and decreases with the size of the group of pigment particles (Fig. 8). While this particular measure of size uses an essentially two-dimensional estimate to represent an essentially three-dimensional parameter, this is not distorting the information to any significant extent. For example, Fig. 15 presents the scattering coefficients plotted against group size and, although the coefficient decreases with size, the PVC is obviously more important than the size. This pattern was expected, on purely theoretical grounds, and thus supports the usefulness of this estimate of the size parameter.

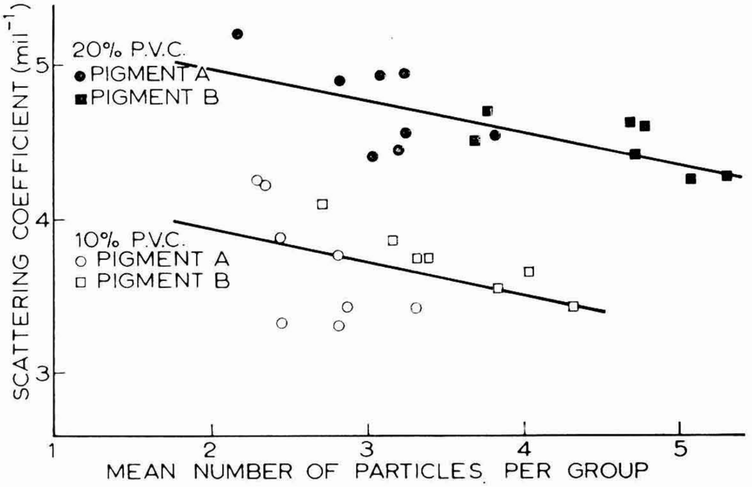
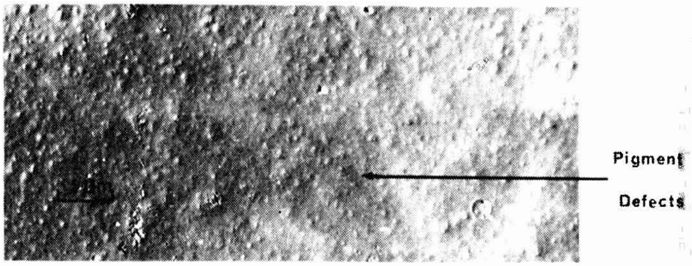


Fig. 15. Scattering coefficient vs mean number of particles per group

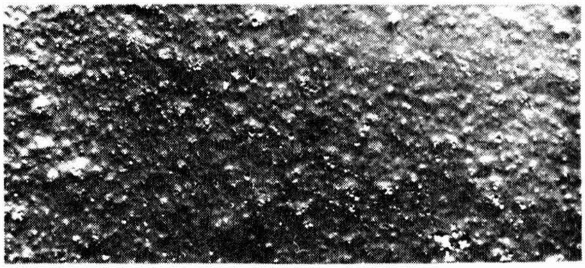
Reverting to Fig. 8, it is obvious that increases in PVC have less effect on gloss than increases in size. Further, pigment A, which has the larger primary crystal diameter, is the more effective at reducing gloss for any particular group size and PVC. Comparing Figs. 8 and 15, it becomes clear that, at this level of dispersion, primary crystal diameter and the size of the groups produced by the dispersion procedure are of primary importance in governing gloss, but of secondary importance in governing scattering coefficient. That is, $k(d\lambda)/d^2$ is increasing rapidly as the size increases. For pigment A, $k(d\lambda)/d^2$ goes from $\sim$1.5 at a size of 2 particles per group to $\sim$8.5 at a size of 3.5 particles per group. A comparable change is observed for pigment B, where $k(d\lambda)/d^2$ goes from $\sim$0.5 at 2.5 per group to $\sim$7.5 at 5.5 per group. In all cases the exponential expression (5) has been assumed. The fact that the values for $k(d\lambda)/d^2$ are not the same for the two pigments at any one group size, is probably due to their different primary crystal sizes.

These values of $k(d\lambda)/d^2$ are much lower than those obtained for the silica additions, as would be expected from the greater efficiency of the silicas. The values obtained can be used to comment on $k(d\lambda)$, the area of zero reflectivity, which is associated with the defects produced by the pigment particles. Despite the quadratic increase in d, $k(d\lambda)/d^2$ increases with increasing group size. This must mean that $k(d\lambda)$ is increasing very rapidly as the number in a group increases, at least over the size range investigated. That is, the increase in the area of zero reflectance is far outweighing the decrease in the number of such areas.

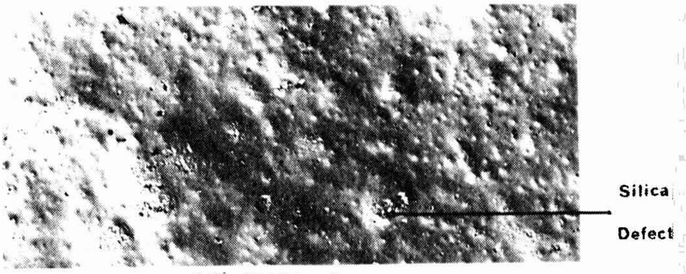
An indication of the relative importance of the actual defect size can be obtained from Fig. 16, which presents surface replicas for some of the paints to which silica was added. The relatively small and ineffective defects produced by the pigment, which is clearly well dispersed, are quite visible. The relatively large, but not very high, defects produced by the silicas are also visible. These large defects must be associated with a large area of zero reflectivity for them



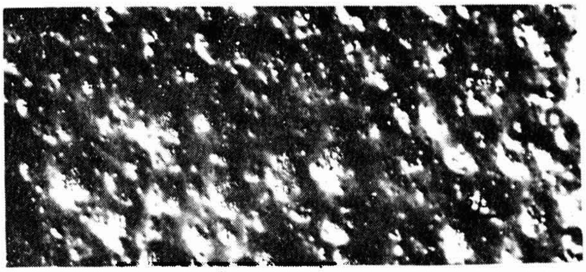
0·3 SILICA C



0·3% SILICA D



2·7% SILICA D



2·7% SILICA E

Fig. 16. Part of typical low magnification surface replicas of paint films with relatively low and high silica additions

to be as effective as they are in reducing gloss. For the pigments, all of the groups of particles interfering with the surface are producing defects with values of $k(d\lambda)/d^2$ on the ascending section of plots, such as Figs. 10b and 11b. The silicas, on the other hand, are giving values much higher, possibly in the region of the peak of such curves.

Conclusion

This work has indicated that there are two components which contribute to the efficiency with which surface defects cause gloss deficiency. The physical size of defects is related to the area of zero reflectivity produced by it in a most complicated way. This area increases very rapidly as the physical size increases at least up to "flat" defects of about 1μm lateral extent. An increase in the number of such defects produces a corresponding decrease in gloss although not a linear decrease.

In the common case of a fixed amount of pigmentary material being present in varying degrees of dispersion, it is likely that, as the dispersion becomes worse, the rapid increase in each individual area of zero reflectivity produced by the larger groups will far outweigh the fact that there are fewer groups present.

Although the presence of an optimum size has not been demonstrated in this work, it has been implied by other workers[7, 8] and the simple theory presented here helps to explain it.

Acknowledgments

The authors gratefully thank their colleagues for assistance in the preparation of this paper, and the Directors of Laporte Industries Limited for permission to publish.

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Discussion at the Torquay Conference

PROFESSOR G. D. PARFITT pointed out that, although the effect of the silicas used in the work on the gloss of the film had been quite large, the author had not given much detail of their characteristics. It had been stated that gloss was directly related to degree of dispersion, which would in turn be directly related to the components present. In particular, if the silica had a particle size appreciably smaller than that of the pigment used, this would play an important role in the flocculation behaviour.

DR J. DUNDERDALE said that considerable difficulty had been experienced in obtaining the particle size of the silica, particularly because of flocculation effects. Electron micrograph sections of the film tended to indicate that the particle size of the silica was less than the pigment, and an interesting point was that the silica particles did not appear to be reduced in size during milling.

PROFESSOR PARFITT commented that the micrographs showed both hetero-and homo-flocculation. It had been shown that the presence of smaller particles could affect flocculation, and he felt that it was important to consider this when adding flatting agents to paint formulations.

Also, in considering the effect of dispersion on surface defects, was the dispersion of particles at the surface of the film the same as that in the bulk?

DR DUNDERDALE replied that there was no reason to believe that the distribution of particles at the surface was any different from that in the bulk of the film. It was believed that solvent-based films, as used in the work, dried from the bottom up; Hence there was no possibility of forming a skin, which could push the particles down and cause a levelling effect on drying.

As had been stated, this work was in its early stages, and much of it was inference, but no attempt had been made to investigate the reasons for flocculation, only to relate the flocculation present to surface defects.

PROFESSOR PARFITT agreed that this was a valid point, but said that he thought it was of interest to consider carefully the surface of the film. Published work had indicated that a thin clear layer was formed at the surface of alkyd films, while in acrylic films, the reverse occurred, and a greater concentration of pigment was found at the surface.

DR DUNDERDALE said that a large number of cross-sections had been examined, and no clear layer was obvious, unless, by "thin clear layer" it was meant that none of the pigment particles was not covered by binder, in which case he would agree. The thickness of the clear layer was the point in question.

MR S. E. MASKERY remarked that the Joyce Loebl disc centrifuge might be of use in determining the particle size distribution of the silicas. However, the various silicas on the market had different structures, and some were more friable than others. Hence a more friable type might break down on dispersion, causing different results.

With regard to the peak heights obtained from the spectrogoniophotometer, he felt that these could be very important in assessing the gloss of a paint at different angles.

DR DUNDERDALE agreed, and said that it was necessary to measure the particle size distribution in the system under investigation, as it might differ from that in the dry state or other systems.

MR D. F. TUNSTALL said that he was surprised to see an apparent lack of variation in scattering coefficient between the two pigments of different primary particle size. Was it possible that errors were being caused by the sectioning procedure when assessing agglomerate size? This was known to occur in some cases, and might give spurious results at differing PVCs. Also, had any allowance been made for the fact that the widely different gloss levels would affect the determination of scattering coefficient for the two systems?

DR W. E. CRAKER replied that the lack of effect of particle size on scattering could be predicted theoretically. Using a combination of Kubelka-Munk and Mie theory, it could be shown that, for distributions of particles having mean diameters between about 0.15μm and 0.3μm, the scattering coefficient was sensibly independent of the particle size. The possibility of errors being caused by the sectioning procedure had been foreseen and a check had been carried out by preparing several dispersions by different methods. It had been found, with all the dispersions, that the degree of aggregation affected the scattering coefficient little, and the gloss markedly, and since the dispersion by each method would not be expected to be the same, this tended to support the conclusions made. He agreed that gloss could affect the scattering coefficient measurements. Some work had been carried out to investigate this, and it was not thought to make an appreciable difference to the results obtained. Using the approach developed in earlier work (*JOCCA*, 1967, **50,** 111) it had been estimated that the maximum effect was in the region of 5 per cent to 10 per cent of the measured scatter.

Next month's issue

The Honorary Editor has accepted the following papers for publication, and these are expected to appear in the December issue.

Papers from the Torquay Conference:

"Effect of pigment dispersion on the appearance and properties of paint films," *by W. Carr*

"Research and development—recruitment, education and training," *by P. Bennett*

"Financial evaluation of research projects," *by A. G. North*

Correspondence

SI Units

SIR—With the present controversy over SI units I consider that the Association should make a decision as to which system of units they wish used in the *Journal.*

In one recent issue, not only did I notice the use of microns and nanometres in successive articles, but also the use of the terms mg g^{-1} and mg/g in the same table of results. If we must have disparity of nomenclature, let us at least insist on uniformity in the one Communication.

I am also disturbed by the growing tendency in the *Journal* for authors to use symbols "willy-nilly" without explanation of the meaning of such symbols or the quantities they are meant to represent.

Please let us have some uniformity at least in this *Journal.*

Yours faithfully,
P. S. Nisbet.
30 August 1971

A. B. Fleming & Co. Ltd.,
Caroline Works, 170 Glasgow Road,
Edinburgh EH12 9BE

EDITOR'S NOTE

The point made by Mr Nisbet is well appreciated, but we do not feel that at this stage it would be appropriate to insist on the use of SI units. There are a number of reasons for this.

Firstly, there is always a period of some months between the receipt of a paper and its publication, it would therefore be necessary to give authors considerable notice that such a step would be taken. To convert all the papers in hand to SI units would involve a great deal of editorial work and could conceivably result in some confusion in points made by the authors.

Secondly, it would not be reasonable to insist on the adoption of these units when some of the industries served by the Journal have not yet adopted metric units. The paint industry itself has only recently started to supply in metric volumes, and some allied industries in which a significant proportion of the membership is found and from which a number of papers for publication are received, have not yet reached this stage. The use of SI units in a paper on a relevant subject might render it largely incomprehensible to readers working on the practical side of these industries.

These and other restrictions have led to the decision that the adoption of SI units, though highly desirable, should be gradual, until such time that it is felt appropriate to insist upon their use in all papers.

Technology of Surface Coatings or Technology of Coatings?

SIR,—Years and years and *years* ago one of your predecessors printed a short letter—not from me—making it clear that only a slack refusal to think could have been responsible for currency being given to *surface coating* as the name for a class of substance.

Anyone has only to look in a decent dictionary (e.g. the "Shorter OED") to see that a *coating* is something put on a *surface*, from which it follows that *surface coating* is one of the crudest and clumsiest tautologies that anyone could possibly compose in so few as two words.

Whence I am horrified to see that in the proposed Professional Grade a typical designation will be *Fellow . . . in the Technology of* Surface *Coatings.* Professional! Really!

May I, as a fairly long-standing Ordinary Member who performed a small service for OCCA during the war, ask for a simple test to be made? Members of the Professional Grade Committee must, I suppose, have many contacts outside the paint industry, which always has taken the line that if "you know what it means" it's all right. Let them ask 20 teachers of English in secondary schools anywhere in England, and if so many as two can be found willing to *support* (not merely swallow) *surface coating* I will buy a hat and eat it.

Yours sincerely,
Neil R. Fisk.

5 Grange Court
Pinner HA5 5QB
17 September 1971

Reviews

EXPERIMENTAL DESIGN SELECTED PAPERS BY F. YATES, FRS. London: Chas. Griffin, 1970. pp. xi + 296. Price £4.20

With the computer as an ever present aid, and textbooks by the dozen available from any public library, the development of statistical designs tends to be ignored. Frank Yates at Rothamstead Experimental Station was one of the most important researchers in this field, and not only did he (together with Professor Fisher) have to develop the techniques, but also to establish their credibility to an often doubting scientific world.

During his years at Rothamstead he trained many practical statisticians, and on his retirement, Cochran, Finney and Healy persuaded him to select a number (12) of his papers for publication in book form.

Your reviewer cannot with any honesty comment on these papers; they are part of the history of statistical design, covering the years 1933–1966. They all demonstrate Yates' ability to define clearly and simply what he is doing and why, and are models of how a paper should be presented. The difficulties which he faced in gaining acceptance for his methods can be gauged from his written replies to questions on his paper IV entitled "Complex experiments."

D. S. NEWTON

PRINCIPLES OF POLYMER SYSTEMS BY F. RODRIGUEZ. New York: McGraw Hill Book Company. 1970. pp. xi + 560. Price: £7.90

This book purports to be an introductory text, but for whom such an introduction is appropriate is not explained in the preface and is difficult to envisage from the substance. It covers a great deal of ground ranging from basic structures of polymers, polymer formation, physical states and transitions, to detailed considerations of viscous flow, mechanical properties, production and fabrication processes, and analysis. Much of this is done extremely well, but a generally laconic and sometimes disjointed style does not make for easy reading. The presentation of fundamentals in the early chapters is often misleading for the beginner, whilst the treatment of more advanced topics demands an expertise unlikely to be possessed by many students and not always provided by a reading of the earlier chapters. Finally, whilst many may feel that this is yet another general text book about polymers which relies too heavily on other secondary sources for its content, others will like it because it provides their chosen cross-section of information—rather as a paint formulator chooses a particular alkyd from the many available because it suits his individual witchcraft.

The brief opening chapter presents some interesting statistics of polymer production and sales. Among these is the observation that the average sales value of plastics in dollars per pound fell steadily throughout the nineteen fifties and sixties despite a monotonic rise in the consumer price index. Equally interesting is the fact that the selling prices of a wide variety of plastics in 1967 decreased linearly with the logarithm of the tonnage produced, almost regardless of the nature, chemistry and complexity of the material. Thus, polyethylene, phenolics, cellulosics, polyacetals and polycarbonate, plotted in this way, fall on the same straight line!

It is not considered appropriate to review the contents in detail, for most of what one expects of a general text book is there, and there are few actual mistakes. The present reviewer found the two chapters on mechanical properties at small deformations and on ultimate properties very good indeed and by far the best in the book. That on fabrication processes is much more comprehensive than is generally found in a work of this kind, despite the rather short section devoted to coatings which relies heavily on the works of Parker and of Nylen and Sunderland. A feature of the work is the presentation of imaginative and searching problems at the end of each chapter, but it is necessary to warn those who would attempt their solution, that not all can be solved by reference to this book alone.

A. R. H. TAWN

Courses available 1971-72

Since publication of the September issue, information has been received from a further college, and details are given below.

Slough College of Technology

Department of Science, Wellington Street, Slough SL1 1YG.

The City & Guilds Paint Technicians Certificate Parts I and II.

Enrolment took place in September; students joining the course after the enrolment date are subject to an additional fee of 50 pence.

Those requiring further information should contact the course organiser, Mr H. Bray, at the above address.

Information Received

(In case of difficulty regarding addresses, members and subscribers to the JOURNAL *should apply for details to Director & Secretary of the Association at the address shown on the front cover.)*

"A study in precision" is the title of a booklet recently published by **Winstones Limited.** The booklet, which runs to 20 pages, most in full colour, describes the processes which are involved in the manufacture of Winstones printing rollers.

The range of *Hunterlab* instruments for appearance measurement is now to be marketed in the UK. **Hunter Associates Laboratory, Inc.,** the American manufacturer of the instruments, has set up a sales outlet in Hertford, from which the complete *Hunterlab* range is available.

Hunterlab has recently introduced three new instruments, the *D25D Digital Colour Difference Meter*, the *D16 Glossmeter*, and the *D48D Glossmeter*. The *D25D* is the latest in the *D25* series, and features automatic digital display of colour values, including polarity. Both the Hunter L, a, b, and CIE x, y, z, values, together with their Δ values, can be selected by pushbutton. Four optical heads are available for the instrument, including the "M" head for circumferential viewing of textured finishes, as used on the earlier *D25* instrument, which is still available. The *D48D Glossmeter* features solid-state circuitry and digital read-out. Three plug-in optical modules are supplied, meeting ASTM D523 for 85°, 60° and 25° measurements respectively. All three modules can be connected to the master unit simultaneously and any one selected by pushbutton. The *D16 Glossmeter* also contains solid-state electronics with digital display. Models are supplied for various viewing angles, meeting the appropriate ASTM or TAPPI specification.

A new, inexpensive, field telephone approved by HM Factory Inspectorate for use in areas which present fire hazards has been developed by **F. W. Reynolds Limited.** The telephone, *Safon Mk. 2 Type GA 0052*, meets the requirements of non-incendive sparking for apparatus used in Division 2 areas. Completely self contained, the instrument houses its own battery, solid-state calling oscillator and transformer. Although light in weight, it is claimed to be very robust. Mercury cells are used, and in the event of a current in excess of 50mA being produced, the battery voltage collapses, making the production of dangerous sparking impossible.

PIRA, the research association for the paper and board, printing and packaging industries, is to hold open days on 10 and 11 November to mark the opening of the new 20,000 sq ft extension housing the paper and board division. Representatives of non-member firms will be particularly welcome, and should contact the secretary of PIRA to give notice of their visit. Details of courses to be held at PIRA for the session 1971-72 have also been released, and may be obtained from PIRA.

The latest in the series of PIRA visual aids, No. 20 "What is a halftone" is designed to give a general appreciation of reproduction methods to those familiar with print as an end product, as well as to students and apprentices entering the printing industry. The visual aid comprises 25 colour slides (35mm) and lecturer's notes, and is available at £7.00 to PIRA members, or £14.00 for non-members.

A multi-client, techno-economic study on radiation curing has recently been completed by **Skeist Laboratories, Inc.,** of New Jersey, USA. The study concentrates on electron beam and ultraviolet curing systems for surface coatings in the USA, and detailed profit opportunities are shown for companies involved in all aspects, from raw materials suppliers to end users. Full details are available from Skeist.

A new high jet black carbon dispersion for colouring latex—particularly carpet backing—and paper and board has been introduced by **International Colloids Limited.** The new dispersion, *Microsperse 26*, is a 38 per cent aqueous solution of a high jet furnace black, and contains a new blend of wetting agents to ensure dispersion stability and aid in obtaining an even shade for the coloured article.

Lennig Chemicals Limited is to manufacture the range of *Paraloid* thermoplastic acrylic resins in the UK, it has recently been announced. Previously imported from Lennig's American parent, **Rohm and Haas,** all the *Paraloids* will be manufactured at Lennig's Jarrow factory. Four products in the range—*Paraloids B44*, *B66*, *B72* and *B82* are already in production at Jarrow, and the others will follow by the end of the year.

Flexaphane GL XC 8000 is an improved version of the **Fishburn Printing Ink Co. Ltd.** catalysed lacquer incorporating "gluability." Designed to meet a market demand for a lacquer that will take adhesives, the new *Flexaphane* is also claimed to have higher heat resistance and better gloss than the previous formulation.

The Building Research Station has published a new reference book "The analysis of concretes" by J. W. Figg and S. R. Bowden. Intended mainly for laboratory analysis of hardened concrete rather than on-site work, the book is available from HMSO at £6.00 per copy.

It has recently been announced that the independent consulting practice in paints and related subjects established by Mr H. R. Touchin is to operate under the title **Touchin Technical Laboratories.** This title has been adopted to accord better with the wide range of services offered and laboratory facilities available. There is to be no change in the general policy and operation of the practice, and the associated practice of **Corrosion Engineering Consultancy** will continue under its present name.

A new type of dry feeder for the accurate handling of relatively small quantities of powdered or granular materials had been introduced by **Paterson Candy International Limited.** The *AW type* dry feeder consists of a feed hopper discharging on to an electrically operated vibrating trough. The material from the vibrating trough is fed at a controlled rate into a pan supported on a pneumatically operated load cell, which is set to tip its contents into a discharge chute when the desired weight is reached. Manual or automatic weight setting is possible.

The feeder can operate at a maximum speed of three tips per minute, the maximum discharge being 300g per minute; weighing accuracy is claimed to be within 1 per cent of the 100g maximum load.

General & Industrial Paints Limited has introduced a new bare metal stopper to the *Glasso* range of refinishing materials. The new material, *Glasso GBS2*, is based on pigmented cellulose and, it is claimed, couples easy, smooth, spreading with fast drying characteristics, to give good flatting and feather edging results.

Work has commenced on a new styrene-butadiene latex plant at Bilbao, Spain, announce **Dow Unquinesa SA.** Scheduled to come on stream in late 1972, the new plant will, it is said, have ample capacity to satisfy latex demand in Spain for several years.

Irish

The efficient use of titanium dioxide pigments in organic compounds

The first Meeting of the 1971-72 session was held at the Clarence Hotel on Friday 17 September at 8.00 p.m. The Chairman of the Irish Section, Mr D. Sharp, introduced the Speaker for the evening, Mr J. G. Hoogerbeets of NV Titaandioxydefabriek Tiofine, Holland, who gave a lecture entitled "The efficient use of titanium dioxide pigments in organic compounds."

There were 19 members and 7 visitors present and a lively question and answer session took place after the talk.

A vote of thanks was proposed by Mr D. Power on behalf of those present.

A.R.

Notes and News

Technical Exhibition

17-21 April 1972

Widespread support

The Exhibition Committee is pleased to announce that applications received at the time of going to press show that support for next year's Exhibition is widespread, and they are encouraged by the number of companies showing for the first time at an OCCA Exhibition. Applications have been received direct from companies in the following countries —Belgium, Canada, Denmark, Finland, France, Germany, Holland, Italy, Sweden, Switzerland and the USA.

Many inquiries have been received at the Association's offices about dates for future Exhibitions. The Exhibition Committee wishes it to be widely known that it has now completed arrangements with Olympia for the holding of the Exhibition for the next three years, the dates being April 1972, May 1973 and April 1974.

Further details will be published in the *Journal* and all members of the Association will be sent copies of the *Official Guide* for the 1972 Exhibition several weeks in advance. Non-members wishing to receive copies of the *Official Guide*, which will be available without charge, should make application to the Association's offices as soon as possible.

The optional Professional Grade for Ordinary Members

As announced in the September issue of the *Journal*, Council has recently introduced an optional Professional Grade for Ordinary Members of the Association. Full details of the regulations were given on pages 916-921 and it is not proposed, therefore, to set these out again, but it is felt that members will be interested to know that, at the time of going to press, 100 applications in all had been received. Amongst these were applications for the Licentiate grade where candidates have to obtain prior approval of a topic for dissertations to be presented to the Committee. Council feels, therefore, well justified in its endeavours to afford members of the Association the opportunity of educational identity with the surface coating industries and urges all senior members of the Association, not only to apply for admission to the Professional Grade, but also to encourage younger personnel to take advantage of this facility. It is hoped that the first list of Ordinary Members admitted to the Professional Grade will be published in the January issue of the *Journal.*

It is felt that Members may like to be reminded that, although the scheme eventually calls for sponsors in each category, since the Association has now been in existence for over fifty years it was felt by Council that present Ordinary members, or Students, of the Association should be allowed the opportunity to apply for admission to the Professional Grade without sponsors for a period of one year, i.e. until October 1972.

Reprints of the regulations are available, together with additional copies of the application forms, from the Association's offices.

Although for the Licentiate and Associate grades candidates can count periods as Students of the Association for the qualifying periods necessary in each case, they have to transfer to Ordinary Membership before applying for admission to the particular grade. Younger members are particularly urged, therefore, not to defer becoming Students of the Association since in any case it takes a certain time to complete the necessary formalities to enrol as a Student or Ordinary Member of the Association. Non-members are therefore reminded that, under the Articles of the Association, those joining in the last two months of the year count their subscription for the whole of the succeeding calendar year and anyone elected in November or December will receive copies of the *Journal* for those months.

Membership application forms are also available from the Association's offices.

London Section

Ladies' Night

The London Section Ladies' Night is to be held on Friday 19 November at the Strand Palace Hotel, London WC2. This is the first time that this venue has been used, and numbers are unfortunately strictly limited. It is essential, therefore, that any Members requiring tickets apply immediately.

News of Members

Mr J. M. Shirt, an Ordinary Member attached to the Hull Section, has recently been appointed technical manager of International Colloids Limited. Mr Shirt will be working mainly on product development.

Mr H. T. Chellingsworth, an Ordinary Member attached to the Midlands Section, has been appointed to the board of Ault and Wiborg Industrial Finishes Limited. Previously executive director responsible for technical services, Mr Chellingsworth now specialises in the technology of powder coatings.

Chemical Society and Royal Institute of Chemistry Inaugural Annual Meeting

The Inaugural Annual Meeting of the new Chemical Society and Royal Institute of Chemistry is to be held in Manchester from 10-14 April 1972. The meeting will be based on the University of Manchester Institute of Science and Technology, but facilities at the Universities of Manchester and Salford will also be used. Ten symposia will take place during the meeting; full details are available from the Chemical Society.

Society of Engineering Science

The Society of Engineering Science has announced that it is to organise its first international meeting in Tel-Aviv, Israel, from 12-17 June 1972. The subject of the meeting is "Pollution: engineering and scientific solutions," and it has been timed so as to be immediately following the first United Nations conference on "The human environment." Full details may be obtained from the Department of Engineering Sciences, Tel Aviv University, Israel.

Register of Members

The following elections to membership have been approved by Council. The section to which new Members are attached is given in italics.

Ordinary Members

BLANCHARD, DESMOND, BSc, 2 Benn Street, Rugby, Warwickshire. (*London*)

BOONCHUA, BANCHIT, BSc, ICI (Thailand) Ltd., KM.5, Chaengwatana Road, Nonthaburi, Thailand. (*Overseas*)

RAFFERTY, FRANCIS JOSEPH, BSc, Anchor Chemical Co. Ltd., Clayton Lane, Manchester, M11 4SR. (*Manchester*)

SAVILL, CHRISTOPHER ARTHUR, BSc, 15 Woodfield Road, Braintree, Essex. (*London*)

SAW, TIONG GOO, BSc, ICI Paints (M) SDN. BHD., PO Box 78, Petaling Jaya, Selangor, Malaysia. (*Overseas*)

SHAIKH, SAMI AHMAD, B.Comm., c.o M/s. Ismailsons Paints Ltd., F/59, SITE Mauripur Road, Karachi-28, Pakistan. (*Overseas*)

SKITT, GEORGE EDWARD, 50 Annesley Crescent, Goose Green, Wigan, Lancs. (*Manchester*)

WHITEHEAD, GRAHAM HARRY, BSc, 7 Stock Orchard Crescent, London N7. (*London*)

Associate Members

NICOL, ALEXANDRA DAVID, Res. and Development, Dulux, Alrode, PO Box 3704, Alrode, Transvaal, South Africa. (*South African*)

SHARP, DAVID JOHN ARCHER, 6 Kingsweston Court, Pretoria Street, Hillbrow, Johannesburg, South Africa. (*South African*)

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication, and in South Africa and the Commonwealth up to the end of the second month.

Monday 1 November

Hull Section—"Some aspects of drying oil technology" by Mr G. Hutchinson of A. B. Fleming & Co. Ltd., to be held at the Queen's Hotel at 7.00 p.m.

London Section/East Ham Technical College course: "Developments in resins for surface coatings" see October issue page 1000.

Tuesday 2 November

Thames Valley Section—Student Group. "Acrylic resins" by Mr A. R. H. Tawn of Cray Valley Products Ltd., to be held in the Main Lecture Theatre, Slough College, at 4.00 p.m.

Thursday 4 November

Newcastle Section. "Hazard analysis—a quantitative approach to safety" by Mr T. A. Kletz of ICI Ltd., HOC Division, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Monday 8 November

London Section/East Ham Technical College course: "Developments in surface coatings" see October issue page 1000.

Tuesday 9 November

West Riding Section. Speaker to be arranged. To be held at the Griffin Hotel, Boar Lane, Leeds, at 7.30 p.m.

Wednesday 10 November

London Section. "Changes in the physical characteristics of paint films in differing weathering environments" by Mr R. L. J. Morris of the Quality Assurance Directorate (Materials), to be held at East Ham Technical College, at 7.00 p.m.

Newcastle Section—Student Group. "Paint formulation" by Mr H. Caddell of International Paints Co. Ltd., to be held at the Newcastle Polytechnic, Ellison Place, Newcastle upon Tyne, at 3.00 p.m.

Thursday 11 November

Scottish Section. Joint Meeting with British Paper and Board Makers' Association. "Amino resins—their use in surface coatings and paper industries" by Mr R. McD. Barrett of BIP Chemicals Ltd., to be held at the St. Enoch Hotel, St. Enoch Square, Glasgow, at 6.45 p.m.

Midlands Section—Trent Valley Branch. "Chromate and phosphate pigments in anti-corrosive primers" by Mr H. F. Clay and Mr J. H. Cox of SCC Colours Ltd., to be held at the British Rail School of Transport, London Road, Derby, at 7.00 p.m.

Friday 12 November

Manchester Section. "The management of human resources" by Mr J. Munro-Fraser of the University of Aston-in-Birmingham, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester, at 6.30 p.m.

Saturday 13 November

Scottish Section—Student Group. "Exploration of the North Sea for fuel" by Mr Junor of BP Chemicals International Ltd., to be held at the St. Enoch Hotel, St. Enoch Square, Glasgow, at 10.00 a.m.

Monday 15 November

London Section/East Ham Technical College course: "Developments in resins for surface coatings" see October issue page 1000.

Tuesday 16 November

London Section—Southern Branch. "Masonry finishes" by a speaker from the Cement Marketing Board, to be held at the Pendragon Hotel, Southsea, at 7.00 p.m.

Wednesday 17 November

Scottish Section—Eastern Branch. "Pollution." Joint meeting with BPBMA in Aberdeen. Further details will be supplied later.

Friday 19 November

Irish Section. "Powder coatings" by Mr Lonsdale of BJN Paints Ltd., to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

London Section: Ladies Night, to be held at the Strand Palace Hotel, London WC2, at 7.00 for 7.30 p.m.

Midlands Section. "Oil-free alkyds" by Mr A. G. North of Cray Valley Products Ltd., to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham, at 6.30 p.m.

Monday 22 November

London Section/East Ham Technical College course: "Developments in resins for surface coatings" see October issue page 1000.

Thursday 25 November

Thames Valley Section. "The philosophy of paint testing" by Mr T. R. Bullett of The Paint Research Association, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks, at 7.00 p.m.

Friday 26 November

Bristol Section. "Quality control." Discussion evening. Panel: Mr W. S. Grainger of Berger Paints, Mr D. S. Newton of British Steel Corporation, and Mr J. R. Taylor of BP Chemicals International Ltd. To be held at the Royal Hotel, Bristol, at 7.15 p.m.

West Riding Section. Annual Dinner Dance, to be held at the Crown Hotel, Harrogate.

Monday 29 November

London Section/East Ham Technical College course: "Developments in resins for surface coatings" see October issue page 1000.

Thursday 2 December

Newcastle Section: "Flame retardant coatings—the whys and wherefores" by Mr A. G. Walker of Associated Lead Manufacturers Ltd., to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne at 6.30 p.m.

Monday 6 December

Hull Section: "Emulsion polymers for exterior paints—a comparative study" by Mr K. A. Safe of Vinyl Products Ltd., to be held at Queen's Hotel, Hull at 7.00 p.m.

Tuesday 7 December

Thames Valley—Student Group: Open invitation lecture to senior members "Microbiology and corrosion" by Dr E. Pankhurst of the Gas Council, to be held in the Main Lecture Theatre, Slough College at 4.00 p.m.

Wednesday 8 December

London Section: "What's bugging your paint" by Catherine E. Skinner, Microbiological Unit, Paint Research Ass., to be held at the South Bank Polytechnic at 7.00 p.m.

Newcastle Section—Student Group: "Instrumental colour measurement" by Mr J. Bravey of British Paints and Chemicals, to be held at the Newcastle Polytechnic, Ellison Place, Newcastle upon Tyne at 3.00 p.m.

Manchester Section: "Continuous production lines for paint manufacture," (provisional title), to be held at the Royal Institution, Colquitt Street, Liverpool at 6.30 p.m.

Thursday 9 December

Scottish Section: "Modern trends in building and building finishes, including paints" by Mr D. K. Barron of the Building Research Station, to be held at the St. Enoch Hotel, Glasgow at 6.00 p.m.

Midland Section—Trent Valley Branch: "A layman's view of paint" by Mr J. R. Bourne of Mebon Limited, to be held at the British Rail School of Transport, London Road, Derby at 7.00 p.m.

West Riding Section: Joint meeting with the Society of Dyers and Colourists, "A funny thing happened to me on the way to the Patent Office" by Mr A. T. Ransom, to be held at the Griffin Hotel, Boar Lane, Leeds at 7.30 p.m.

Friday 10 December

Irish Section: Ladies Night: "Reminiscences" by Dr F. Stoyle of Protem (Ireland) Ltd., to be held at the Clarence Hotel, Wellington Quay, Dublin at 8.00 p.m.

Saturday 11 December

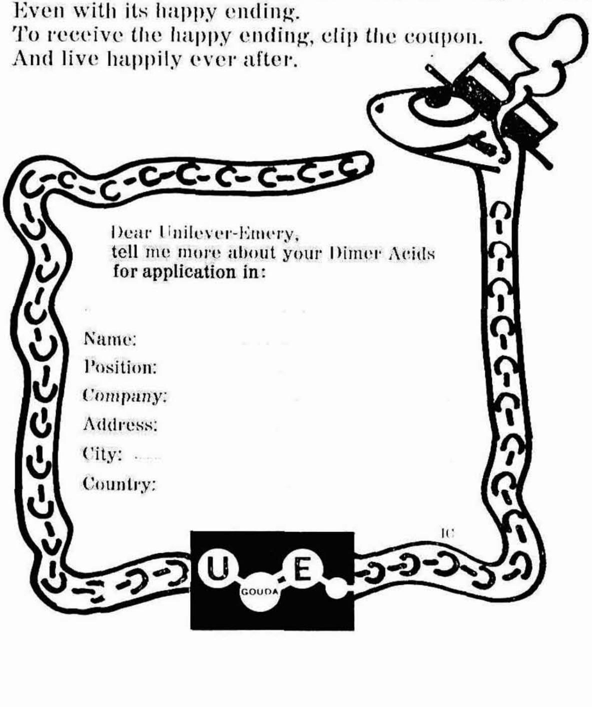
Scottish Section—Student Group: Joint meeting. "Organic pigments for use in printing inks," by Mr D. White of Farbwerke Hoechst AG, to be held at the St. Enoch Hotel, Glasgow, at 10.00 a.m.

Monday 13 December

London Section: Joint meeting with Colloid and Surface Chemistry Group of the SCI, "Colloidal aspects of colour printing" by Dr W. Carr, of Ciba-Geigy (UK) Ltd., to be held at 14 Belgrave Square, London SW1, at 6.00 p.m.

Wednesday 15 December

Scottish Section—Eastern Branch: "Inter-personnel relationships" by Mr R. M. McKenzie, of the Department of Business Studies, Edinburgh University, to be held at the Carlton Hotel, North Bridge, Edinburgh at 7.30 p.m.


U
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GOUDA

introduction to paint technology

second edition with additional chapter

The sales of this Association publication now exceed 13,000, and because of continuing high sales of the second edition, and the need for a work of reference to be constantly abreast of the latest developments in its field, the Council of the Oil and Colour Chemists' Association has authorised the addition of an eleventh chapter to the "Introduction to Paint Technology." Entitled "Recent Developments," the Chapter incorporates up-to-date information on the latest advances in the technology of the paint and allied industries.

This addition will help the "Introduction to Paint Technology" to maintain its position as an invaluable aid to young entrants into the industries and to marketing and other personnel requiring a basic knowledge of the principles and techniques of surface coating production and application.

new chapter

The new chapter is subdivided into three sections—

resins and media

Including polyester, epoxy, polyurethane resins and developments in water based paints, vinylics, etc.

application techniques

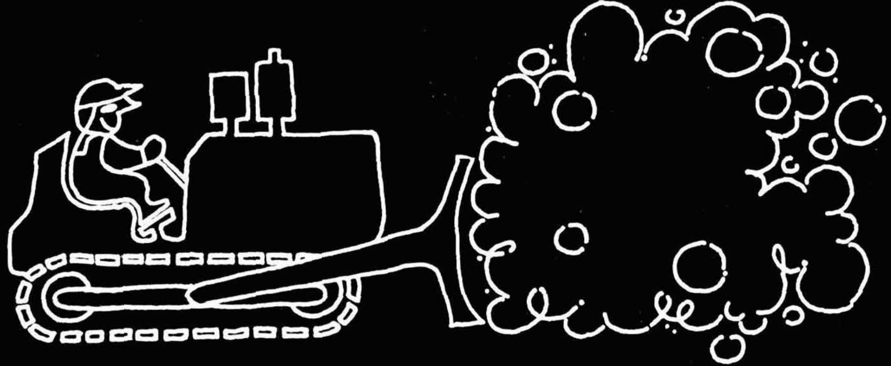
Including electrodeposition, powder coatings, strip-coating, aerosol spraying.

instrumental testing and control methods

Including colour measurement, viscometers, brushability, hardness, film thickness, weatherometers, and use of computers.

The book contains 204 pages including 11 line diagrams, 8 photographs of common paint defects, and comprehensive index. Copies can be obtained from the Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London E.C.2, price £1 (post free).

There is an easier way of removing foam.



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FOAMASTER * New stable, uniform anti-foaming agent. In paints, recommended for use in standard latex systems as well as newer coating systems based on PVA/Acrylic, ethylene vinyl acetate, and water soluble alkyds. Also used in manufacturing and compounding synthetic latex systems.

FOAMASTER * B 100% active defoamer, showing greater dispersibility than Foamaster. Effectively defoams emulsions and suspension polymerizations and is specifically applicable to stripping PVC as well as latex polymers in addition to controlling foam during compounding.

FOAMASTER * NS Liquid non-silicone defoamer for latex systems, suitable for latex paints, including butadiene-styrene, acrylic and PVA types. Also suitable for latex adhesives.

FOAMASTER * P Unique product for defoaming during polyvinyl alcohol production, added after the synthesis step. Available also in concentrate form for high temperature defoaming.

FOAMASTER * R Excellent defoamer for semi-gloss systems without colour sacrifice, long lasting foam control. Suitable for control of foam during manufacture and compounding of synthetic latex systems.

FOAMASTER * S A more rapidly dispersible version of Foamaster R. Uses are broad in scope with semi-gloss systems a major application. Product can be added to storage tanks to eliminate foam in subsequent handling operations. Can also be used during production and compounding of synthetic latex.

FOAMASTER * W A liquid defoamer for use with all the major latex paint systems, also used as a defoamer for acrylic and polyethylene floor polishes.

FOAMASTER * T Excellent defoamer for tint base paints without giving colour loss, should be added to the grind stage before colour addition.

You'd like to meet Nopco's other defoamers? Or find the one that best answers your particular problem? We'll be glad to send detailed literature. And remember — the Advisory section of the Nopco Foam Removal Service is always at your disposal.

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MARKETING DEPARTMENT
Paints Division

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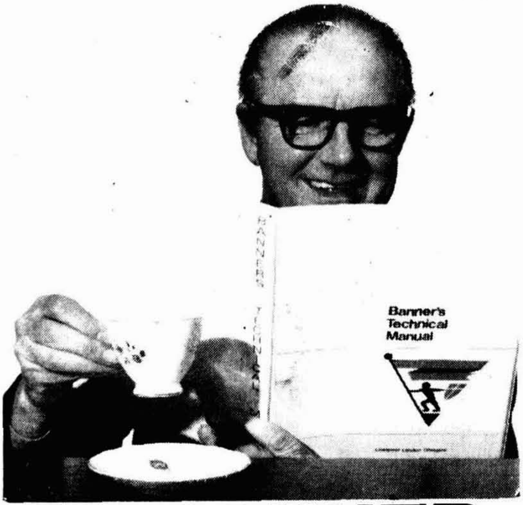

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Oil & Colour Chemists' Association

PAINT TECHNOLOGY MANUALS

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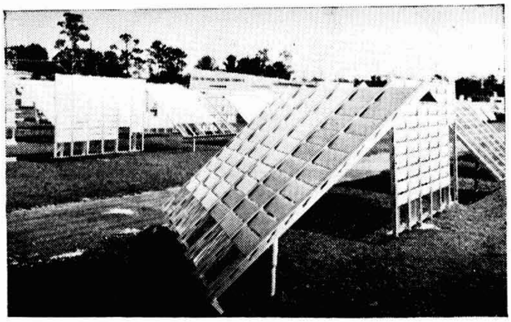

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